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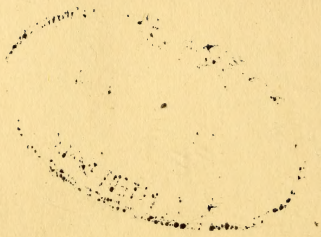

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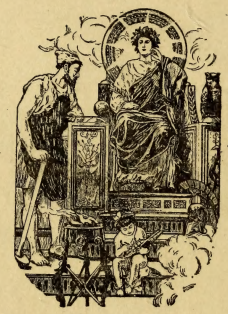

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SEMI-ANNUAL REPORT

OF

SCHIMMEL & Co.

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MILTITZ

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List of abbreviations.

d = specific gravity.

$d_{20°}$ = specific gravity at 20°, compared with water at 15 .

$d\,\frac{20°}{4°}$ = specific gravity at 20°, compared with water at 4 .

$\alpha_{D20°}$ = optical rotation at 20°, in a 100 mm. tube.

$[\alpha]_D$ = specific rotation.

$n_{D20°}$ = index of refraction at 20°.

Sol. p. = solidifying point.

M. p. = melting point.

B. p. = boiling point.

n = normal.

Acid no. = acid number; ester no. = ester number; sap. no. = saponification number.

g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Miltitz near Leipzig, April 1, 1909[1]).

It is unfortunately impossible to say much that is cheerful about the period reviewed in the pages of the present Report. As we were already compelled to place on record in November last, the year 1908 moved under the sign of economic depression, which in the nature of things made itself especially severely felt in the principal industrial countries, viz., Germany, Great Britain, and the United States. The continual decline in value of raw materials hampered enterprise in all circles where our products are consumed, and the mere fact that in spite of the favourable conditions which prevailed in the money market, important transactions in the staple articles of our trade were entirely wanting, should be sufficient proof that among those concerned confidence in the proximate revival of the general state of trade was still looked for in vain. In any case, those optimists have been proved to be mistaken who prognosticated from the return of sounder economic conditions in the United States an immediate reaction upon our European markets; for in spite of the favourable reports which have been received from America since the beginning of the present year (especially as regards transactions in our branch of industry) it is unfortunately true that as yet there can be no question of any noticeable improvement in business in this particular quarter.

So far, the wounds which have been caused by the financial crisis in all circles where our goods are consumed have only been partly healed, and the consequences of the general falling off in values, which have found expression in serious losses on the stocks remaining over from the record year 1907, are being felt everywhere. It is only within the last few months that the sales have again reached figures denoting a tolerably healthy demand for consumption, and no doubt many more weeks will elapse before it will be possible to report of a genuine revival of interest on the part of consumers.

The decline in the exchange of commodities belonging to our branch of business with foreign countries finds expression in the fact that the imports of essential oils[2]) into Germany in the year 1908

[1]) The commercial part of this Report has been compiled during March.
[2]) German Official Statistics of Merchandise, No. 353 b and c.

amounted only to 911,300 kilos against 1,498,600 kilos in the year 1907, while the exports fell from 491,700 to 445,300 kilos.

The considerable decline in the imports is traceable to the small demand for those varieties of oils which are imported by Germany from abroad, either for the purpose of manufacturing them into perfumes, or for refining. The further course of business in the current year will depend in the first place upon the question whether it will be possible to remove finally the state of political tension which has been the chief topic of conversation for many months and which threatens to light the torch of war in Eastern Europe. If diplomacy should succeed in suppressing the danger of war and if our friendly relations with the other European Powers (relations which have recently been improved by our understanding with France in the question of Morocco and by the visit of the King of England) should be maintained, the hope for a return of better times will doubtless be fulfilled. In such an eventuality, the only thing to be wished for is that the improvement should not occur too rapidly, as otherwise the danger of renewed reaction would be too great.

Unfortunately the economic condition of Germany continues to be influenced by the unfavourable situation of the Imperial finances and the recurrence of adventurous proposals of financial reform, which are a sequence of this condition. In the interests of our own industry it is especially desirable that a final decision will soon be reached with regard to the Spirit Bill, in order that this much-debated subject may at last be cleared up.

In spite of the generally unfavourable state of business, our Austrian branch in Bodenbach (Bohemia) was comparatively well at work, and it cannot be said that the ancient race-hatred between Bohemians and Germans has exercised a really unfavourable influence upon business in the districts where it prevails, although, especially within the past few months, it has broken out on repeated occasions. The boycotts proclaimed by either side against the other mostly came to nothing, which is a sign that the movement does not affect all classes of the population to an equal degree. The alarming reports about the conflict with Servia, with all the consequences that might follow from it, have of course occupied the principal place in public interest in Austria recently. Although the result of a warlike conflict between the two States could not for a moment be in doubt, such a solution of the dispute might have effects upon the European Peace, the extent of which it would be impossible to foresee. We are still awaiting the new Austrian Spirit Bill already referred to in our last Report, but it has lately been asserted that it may be expected to come into action next autumn.

The commercial and industrial depression in Great Britain, to which we referred in our November Report, has unfortunately not undergone

any marked improvement since then. Business generally has been exceedingly slack and dragging, with comparatively small transactions, and especially as regards the soap industry, very little news of an optimistic character can be reported. On the contrary, in this branch of business competition has become even more keen, with the result that the few large transactions which were carried into effect had to be closed at prices which, in the case of first-quality goods, can hardly pay any of the parties concerned. England continues to suffer perhaps in a larger measure than any industrial country on the Continent from the after-effects of the American crisis, and this fact, taken together with the far-reaching radical, nay, almost socialistic legislation of the last few years, which can hardly be justified financially, no doubt paralyses all trade and traffic, with the result that a healthy development of business enterprise appears to be downright unattainable.

A comparison of British oversea-trade in the year 1908 with the foreign trade of the competing Nations (among which, we may remark in parenthesis, Germany appears to have lost the least ground) may here be of interest. The decline in exports was as follows[1]): —

From the United Kingdom . .	11,4 %
„ „ United States . . .	8,7 %
From France	5,8 %
„ Belgium	4,3 %
„ Germany	1,4 %

Australia continues to occupy the principal position of interest among the British Colonies. According to the Report of the Hamburg Chamber of Commerce, the decline in the price of wool has caused a serious want of available capital in that country, and even at the present time the scarcity of money has not been quite overcome. German exports to Australia have, moreover, been injuriously affected by the preferential duties in favour of the Mother Country established under the Australian Customs Tariff, which was provisionally applied last year, and which has since come into action. The sale of German goods is further unfavourably affected by the absence of goodwill (we quote from the above-mentioned Report) which is often shown in Australia towards German trade and German merchandise. So far as our own experience goes, we are unable to give an unqualified endorsement to this view, for even under the new Customs Tariff the sale of our manufactures so far has continued to develop in an entirely satisfactory manner.

The final settlement of the Morocco question, which has so frequently threatened to destroy our friendly relations with France, has been received everywhere with lively satisfaction. Particularly in our

[1]) Compare Report November 1908, 5.

industry, which has gradually created for itself a leading market in the important neighbouring country of France, every step is welcome which brings the two nations closer together economically. Of course the future alone can show in how far the peaceful settlement of this question will influence the general relations between Germany and France. In any case it is to be regretted that simultaneously with this settlement another problem has appeared, which must unfortunately be regarded as seriously endangering the commercial relations between France and Germany after having been built up with so much trouble. We refer to the new French Customs Tariff, in which it is proposed materially to increase the Customs duties upon almost all articles in our branch of business. Great Britain has already protested sharply against the proposals of the French Customs Commission which are obnoxious to trade, and we trust that in case no means should be available of taking action against the proposals by diplomatic proceedings, the *Comité Commercial Franco-Allemand* in Paris will at any rate do its utmost to prevent the French Protectionists from being victorious. It can certainly not be maintained that under the protection of her Customs Tariff France has undergone a particularly remarkable industrial development, for it can be proved without doubt that so far as capacity of output is concerned, French industry is very far behind that of Germany and England. The trade between France and Germany has of course suffered during the past year as a result of the general depression. According to the *Documents statistiques sur le Commerce de France*, it reached the following figures (in 1000 fr.): —

1908		1907	
Imports	Exports	Imports	Exports
626 340	640 876	638 157	649 693

Referring to the new French Pharmacopœia discussed in our last Report, we may here mention that by Decree of the French Government dated 17th October 1908, a period of transition of 8 months — that is to say up to May 15th 1909 — has been fixed, at the end of which all medicinal preparations used in France must comply with the new conditions.

In Spain, the condition of affairs in those branches of business in which our articles are employed, continues to be by no means satisfactory, notwithstanding that the proposals for the spirit tax reform have in the meantime come into force. The Spirit Bill which was enacted many years ago by Osma and the provisions of which have had far-reaching consequences, has at last been replaced, on the 10th December 1908, by a new Act. This measure possesses certain improvements upon its predecessor, but most of the old disadvantages have been retained, and several important new ones have

been added. The advantages of the Act are the conversion of the varying duties which formerly prevailed, into a uniform duty, which has been reduced to 20 pesetas for spirits of wine, and 50 pesetas for industrial alcohol per 100 liters of 90 to 95°, the previous duties having averaged about 60 and 110 pesetas respectively. On the other hand, however, the Act has created untenable conditions, and has caused great confusion, by prohibiting pharmacists, druggists, etc., from purchasing or retailing essences and oils which are used in the manufacture of brandy and liqueurs, and compelling the distillers to buy such articles directly from the manufacturers. As a result of protests, concessions were made to pharmacists, perfumers and confectioners, and as it seems hardly likely that druggists can be permanently kept from sharing in these concessions, it follows that the prohibition above referred to has in point of fact become a dead letter even at the present time. But the complications and delays remain in existence to their fullest extent, and these are increased by the fact that often the Authorities themselves do not know how to interpret the letter of the Act. Through our General Agency in Madrid we immediately took the necessary steps to be able to do justice to the requirements of the trade in our articles in Spain under the new conditions prevailing, and we hope soon to be able to report a satisfactory improvement in business.

The provisions of the new German Commercial Treaty with Portugal have not yet been published, but in the meantime the unanimous opinion with regard to it is one of disapprobation. It would really be incomprehensible if German diplomacy should surprise the Nation with a treaty, the advantages of which, as is said to be the case, are entirely on the side of the other party.

Our Eastern neighbour Russia has further recovered from the wounds of the war and the now suppressed revolution. The gallows, however, continues to do its work there, and the prisons are overcrowded; but if the Duma should succeed in acquiring the confidence of the country, the economic revival of this mighty Empire may perhaps be assured. Unfortunately, the political situation in Russia is very closely connected with the Balkan question, and it will depend upon the solution of the Servian conflict whether the blessings of Peace abroad and at home — which have been attained at such heavy sacrifices — will or will not continue to be enjoyed.

With regard to the Scandinavian countries, all that has to be reported is that preliminary steps have been taken in Sweden for subjecting the Customs Tariff to revision before negotiations are commenced for the renewal of the Commercial Treaty with Germany of 1905, which expires next year. Unfortunately, this revision is not likely to be carried out without a number of increases in Customs

duties; but it is to be hoped, for the sake of Swedish industry, that the products of our industry, seeing that they count among the raw materials, shall at any rate not be made subject to higher duties than are now prevailing.

Nothing special can be reported with regard to our intercourse with the Balkan States, and it will be desirable to suspend all expressions of opinion as regards the future of this market until the Servian question has been finally solved. In Turkey, the introduction of a Constitutional régime is still too much in the state of transition to make it possible, at this early period, to point to any beneficial results from this measure of civilisation, or to the recovery in a material sense of the Nation under the sway of the now ruling Young Turkish Party.

The other consuming countries in Europe offer no occasion for special comment; but we cannot conclude this part of our review without a reference to the tragic occurrences in the Far South, the news of which horrified the world at Christmas time. Messina and Reggio, two flourishing cities, have fallen victims to the catastrophe of an earthquake, the like of which is not recorded in the history of the world, and without any presentiment of disaster, thousands of the inhabitants have met their death under the ruins. The entire civilised world deplores with Italy the loss of so many lives, and extends its sympathy in their misfortune to the few remaining survivors, nearly all of whom have lost home and chattels. All our readers know the important position occupied by the two severely tried cities in the trade in Sicilian and Calabrian essential oils, and all will understand that the catastrophe has necessarily resulted in changes in the commerce of these products, the effect of which we are as yet quite incapable of surveying. To our great delight we are able to report that our esteemed friend, Mr. Eduardo Jacob, who has also been our valued collaborator in these Reports during several decades, has been fortunate enough, together with his family, to escape a tragic fate; and we are glad to take this opportunity of again sincerely congratulating him upon his wonderful escape. Mr. Jacob has supplied us with a report which at last enables us to give an authentic account of the condition of things in the regions affected by the earthquake, and in view of the difficult conditions under which his report was composed, we owe him our especial gratitude.

The hope which we expressed in our last Report that in accordance with the experience in previous Presidential Elections, business in the United States would revive immediately after the close of the Electoral campaign, has not been fulfilled in its entirety. During the closing months of the year also there was no real recovery in business-transactions, although a marked feeling of confidence had taken

possession of all commercial and industrial circles since it had become known that the Republican party would remain at the helm, — that is to say, that the contest between Taft and Bryan had been decided in accordance with the wishes of the Eastern States, whose interests are principally connected with foreign trade. Our New York Branch informs us that during the first two months of the New Year business has been extraordinarily animated, and from this fact it draws the satisfactory deduction that trade and traffic are positively, although slowly beginning to revive. Unfortunately, a new spectre has arisen in the form of the impending revision of the Customs Tariff, which is to be carried out as a matter of urgency by the new President. This event is not looked upon without apprehension in all industrial circles in Germany, as it threatens to block the revival of commercial relations with the United States. For the present nothing can be said as to the extent to which various classes of industrial products will be affected by changes, and the answer to the question whether or not the revised Tariff contemplates increases in the Customs duties upon our essential oils and perfumes, must still be left to the future.[1])

It is a matter of especial satisfaction that a Treaty has recently been entered into between the United States and Germany, in which both countries grant each other complete freedom in the matter of the exploitation of patents, and by virtue of which inventors as well as owners of patents will enjoy equal treatment in both countries. The text of the agreement will only be published when the Treaty has been ratified by the Senate. In any case, this result of mutual good-feeling will be warmly applauded, especially in view of the injury done to German inventors and patentees by the compulsion to work their inventions in the country itself, such as in Great Britain.

The statistics published after the close of the year 1908 proved that, both as regards foreign trade and industrial production in the

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[1]) Our New York branch mailed on March 31st the following supplementary information: —

"According to the official text of the Payne Tariff Bill, a number of important Essential Oils have been omitted from the Free List, which would bring them under the general head of «Unenumerated Essential Oils» at 25 % ad valorem.

"The striking feature in the selection of these oils, none of which are manufactured in the United States commercially, finds ready explanation in the strong desire of the originator of the Bill to provide revenue.

"However, there is an almost endless discussion pro and con (already well started) to be looked for, and whatever the end may develop, its intermediate waste of time, and concommittant uncertainties, will seriously disturb not alone the market of the United States, but also of the whole World.

"It is doubtless of great importance for the manufacturing interests of the United States to retain certain Essential Oils on the Free List, but we deem it, under the present tentative condition of the Payne Bill, futile to point out, beyond the above general reference, certain other inconsistencies affecting our line."

United States, 1908 must be regarded as a year of retrogression compared with 1907, although the last quarter of 1907 also suffered from economic depression. The total imports of the United States in 1908 were of a value of $ 1.116.000.000 against $ 1.423.000.000 in 1907, showing a decline of $ 307.000.000, or 21 %. The total exports from the United States in 1908 were $ 1.753.000.000 against $ 1.923.000.000 in 1907, so that the falling off on the year amounted to $ 170.000.000, or 8,8 %. It is chiefly owing to the heavy exports of copper, showing a surplus of 295.000 tons, that the decline in exports has been limited to 8,8 %. The imports of New York, which consist chiefly of manufactured goods either for consumption or for use in industrial processes, has fallen by $ 188.000.000, or 25 %, and the receipts of the Customs in New York were $ 3.600.000, or 17 % below those of 1907.

These data, which we take from the report of the Commercial Expert at the German Imperial Consulate-General in New York, are too clear to need comment, and show the past business year to have been an entirely unsatisfactory one for the United States.

Although in the Argentine the decline in the price of wool, an article of enormous importance for that country, has disturbed industrial progress, the excellent harvest, the produce of which has found a ready sale, has more than recompensed for the loss on wool. The heavy stocks of imported goods, which at first threatened to bring disaster, were soon cleared, and a healthy business demand was developed, in which our industry has also taken its share.

In Uruguay similar conditions prevailed, except that in the first half of the year the unfavourable state of the wool market was still more heavily felt there. The merchants in the interior of the country passed through serious times, and the slowness with which money was paid in, as well as a general disinclination for business, reacted upon the import houses in Montevideo. Recently confidence in the future has been regained, as the harvest prospects are good, and the purchasing power of the population of the back-country may consequently be considerably increased.

As a matter of course, the general crisis has not passed over Brazil without leaving an impression, and the sales of goods in the interior of the country were occasionally seriously impeded. In the Northern part of the Republic business was especially affected by the fall in the price of india-rubber, and in Central Brazil by the increased export duty on coffee. But as towards the end of the year the rubber market improved again and as the further extension of coffee plantations is being put a stop to by the introduction of rice cultivation, there is every appearance that better times are in store.

In the Official *Jornal do Commercio* of January 30th 1909, the summaries relating to the foreign trade of Brazil in the past 3 years,

which had appeared in previous issues, are completed by the addition of official statistics dealing with the month of December. The increase in the value of the exports in December 1908 as compared with December 1907 was about £ 1.400.000, or 39 %. On the other hand, in December 1908 there has again been a heavy decline in the imports amounting, in round figures, to £ 1.100.000, or over 40 %. The total results are as follows: —

	1906 £	1907 £	1908 £
Value of Exports	53059470	54176898	44094992
Value of Imports	33204041	40527603	35491410
Active Commercial balance in the exchange of commodities	19855429	13649295	8603582

The state of trade in Chile during the past year has given small cause for satisfaction, owing to the events of the two preceding years, such as earthquakes, excess of speculation, and the general commercial crisis. The rate of Exchange fell to a point which had never before been reached (about $7^3/_4$ d.), from which it only recovered towards the end of the year up to about $12^3/_4$ d. The over-supply of the market with all kinds of import articles — among others particularly by the consumers of the products in which we are interested — brought about an extremely sluggish condition of business, yielding very little profit and occasionally being altogether at a standstill. It is true that in the course of the past year three factors — viz., a good harvest, which realised satisfactory prices on account of the depreciation of the currency; secondly, an increased output of copper, notwithstanding the lower prices; and thirdly, a considerably diminished importation, contributed to counteract a further worsening of the general state of trade; but unfortunately a decided and lasting improvement still appears to be far distant. In the neighbourhood of Valparaiso and Santiago the crop this year has been a failure on account of drought, and in the Northern part of the country many of the nitrate works are suffering from over-capitalisation or mistakes in management, although the prices of nitrate of soda have not been unsatisfactory. It is probable that only the renewal of the Nitrate of Soda Trust (if this should come about) would again bring some improvements in the prospects of the financially weak companies, which otherwise will have to stop working in face of the competition of the better-situated older concerns. Another cause why careful business people are adopting a waiting policy with regard to Chile lies in the danger, which is still threatening, that in spite of the bad economic condition and notwithstanding its many opponents, the Act on the re-introduction on 1st January 1910 of the Gold Standard (18 d.), is strictly carried out. It is evident that the autocratic, untimely, and entirely doctrinal enforcement of this Act (which no doubt was decreed with the best

motives) would be attended with the most serious consequences in the thoroughly altered conditions which prevail. This has been sufficiently shown by the example of the Convention of 1895, which was also artificially arranged and which ultimately collapsed in 1898, after 3 years of stress. Under such economic conditions the re-building of the city of Valparaiso on a modern plan is only being slowly completed. Moreover, the many opponents of the scheme for the construction of a new harbour have succeeded in causing this project — which is of such extreme importance — again to be deferred for an indefinite period. As a result of the enormous decline in the imports and thanks to the united efforts of the shipowners and Insurance Companies, it has been possible again to restore the necessary order and despatch in the loading and discharging of ships and in the Custom House work along the entire coast; and it is therefore probable that the complaints which have been made on this score for so many years may soon cease altogether. After the settlement of its differences with Peru in the matter of the delimitation of the boundary line, the satisfactory solution of the question of the currency, and the brightening of the prospects of the nitrate industry, a time of vigorous economic revival may again dawn for Chile, notwithstanding the prognostications of the pessimists, who less than a year ago indulged in the darkest prophecies.

On the subject of the soap business in Cuba, an American Consular Report contains a short article which possibly may induce our friends in the toilet soap branch to give increased attention to Cuba as an export market. It is stated that practically all the soap which is used in Cuba is imported, local manufacture being chiefly restricted to the preparation of highly scented toilet soaps. The annual imports of common soap in bars amount to about 9000000 lbs., of which about 12 % come from the United States, 80 % from Spain; and the rest mostly from France. Of toilet soap, about 150000 lbs., in round figures, are imported; of this 50 % come from the United States and 45 % from France. The imports of all other soap together amount to approximately 325000 lbs., of which 75 % are from the United States and 20 % from France.

With regard to the economic condition of Japan and the prospects of German trade in this interesting market, opinions vary profoundly; but it is an undeniable fact that the financial condition of the people of Japan has been seriously injured by enormous increase in taxation during the last few years, and that the purchasing power has been greatly diminished among all classes. The country will also continue to suffer for a long time from the results of the unscrupulous exploitations on the part of industrial speculators, to which we have already referred on previous occasions. The prevailing low prices in all its

principal articles of export, such as copper, silk, camphor, etc., have greatly diminished the profits of the export trade. In addition to this, the exports to China — which country forms the principal outlet for Japanese industry — continue to be halting and even threaten to degenerate into an entire boycott of Japanese products. All these facts contribute to make the condition of trade look by no means rosy; but on the other hand, less pessimistic reports are not wanting, and these indicate a gradual, albeit slow, improvement of the economic conditions. It is, for example, regarded as a favourable factor that the rice crop of 1908 has been an extremely good one, as a result of which the import of rice (the staple food of the Japanese) from Burmah and Tonquin has considerably decreased. In forming an opinion of the import figures, which we quote below, this not unimportant item must be allowed for. Our own experience of the last few months makes it impossible for us to deny that there has been a perceptible improvement in business, which we trust will continue. In one of the recent issues of the *Ostasiatischer Lloyd*, we find a few interesting figures relating to the Foreign trade of Japan. According to this, the total value of Japanese trade with foreign countries was as follows: —

Year	Exports	Imports	Total of foreign trade
1903	311212000 yen	332119000 yen	643351000 yen
1904	341112000 „	384586000 „	825678000 „
1905	344368000 „	500001000 „	844369000 „
1906	423754000 „	418784000 „	842588000 „
1907	430516000 „	494192000 „	924708000 „
1908	373796000 „	435687000 „	812483000 „

In the course of the past year both exports and imports have declined considerably, but whereas the exports have almost gone back to the figure of the year 1905, the imports (not counting the year 1905, when Japan was at war with Russia) were the highest, with the exception of the year 1907.

As an appendix we bring an interesting paper "On the examination of the Essential oil of *Blumea balsamifera* D. C.", by Mr. Richard Jonas, of Brussels. This examination has been partly carried out in our Laboratory.

We also call especial attention to the "Solubility Table of the most frequently used Odoriferous Substances", which, at the instance of some of our clients, we have caused to be prepared (page 142).

Commercial notes and scientific information on Essential Oils.

Almond Oil, bitter. We refer below to the position of the market in this article.

Almond Oil, pressed from almonds, Ph. G. IV. Our sales of this specialty still continue to increase, and at times the demand has been so great that our output was unable to keep pace with it. Generally speaking, the prices of almonds have undergone no change, for fortunately the rumour that about 8,000 bales of almonds had been destroyed in the catastrophe at Messina proved to be exaggerated, and the advance in prices which resulted thereby was consequently only a passing one. The producing districts in Sicily, which are in the neighbourhood of Girgenti, have fortunately remained unaffected by the earthquake. Efforts have recently been made in Apulia, to increase the demand for the article, and reports have been spread, with this end in view, that there has never been any instance of three good harvests in sucession. Moreover, it is said that owing to the drought which prevailed last year the plantations have seriously suffered in parts.

Almond Oil, pressed from apricot kernels. Since apricot kernels have become an article of speculation, it grows more and more difficult to give a commercial report on this commodity. The fear expressed in our last Report that a fresh effort would be made to drive up the prices to the high level which they reached in the course of the summer has fortunately not been realised, for which no doubt the general lack of enterprise is the chief reason. It is to be noted that not only in Damascus, but also in all other districts where apricot kernels are produced, the stocks were very much reduced towards the end of the year, and even in California, where a bumper crop was talked of as early as the spring of 1908, nearly all the supplies have gone into consumption. The stocks in the hands of middlemen in Hamburg, Marseilles, Genoa and Trieste were also practically cleared at the close of the year, with the result that prices rose to about 78 marks per 100 kilos. If a more lively demand should now ensue, — a contingency which, however, is hardly to be expected in view of the general state of business — it is not impossible that the speculators may gain the upper hand and that we may be face to face with a scarcity similar to that which prevailed a year ago. At the present time it is still impossible to form an opinion as to the result of the current year's crop in the principal growing districts, Syria and California; and it is therefore quite out of the question to

give even a guess at the further course of the market. In any case the quotations of our almond oil pressed from apricot kernels, which as a result of large stocks we have been able to reduce slightly, are scarcely likely to undergo a further reduction within the near future. The prices of essential oil of bitter almonds have remained unchanged, and the fact that we are never able to accumulate any stock of this article is sufficient proof that we are gradually succeeding in maintaining our position in competition with cheap and adulterated qualities.

With regard to the theories on the course of the decomposition of amygdalin by emulsin, represented by Feist and Rosenthaler respectively and referred to in our last Report[1]), further communications have been published by both authors.

K. Feist[2]) is unable to see in Rosenthaler's experiments a disproof of his view that in the course of the splitting-up, primarily d-benzaldehyde cyanohydrin is formed. He regards the action of the emulsion as a reversible catalytic process: d-benzaldehyde cyanohydrin + emulsin $\rightleftarrows$ benzaldehyde + prussic acid + emulsin.

L. Rosenthaler[3]) asserts that he merely regards Feist's proofs as insufficient, leaving the question of the accuracy of Feist's theory an open one. In another detailed treatise on asymmetric syntheses effected by enzymes[4]) he reports more fully on his researches, of the results of which the following is a synopsis: —

The synthesis of d-benzaldehyde cyanohydrin from benzaldehyde and prussic acid by the action of emulsin is effected by a constituent (s-emulsin) which differs from that upon whose action the hydrolysing property of emulsin is based (d-emulsin). This s-emulsin possesses enzymatic characteristics and as regards its action an optimum could be found according to time and temperature. Apparently the s-emulsin is either used up in the synthesis, or it passes into an inactive phase. During the experiment it was not decomposed by chloroform or benzaldehyde, although the last-named combination showed noxious effects. In any case, the reaction (the course of which was influenced by varying quantities of the reagents and by variations in the execution of the experiments), proceeds as follows. In the first place the prussic acid enters into a loose combination with the optically active constituent of the emulsin; next the benzaldehyde attaches itself to the residual prussic acid of the compound, forming an asymmetric carbon atom;

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[1]) Report November **1908**, 14.
[2]) Arch. der Pharm. **246** (1908), 509.
[3]) Ibidem 710.
[4]) Biochemische Zeitschr. **14** (1908), 238. Quoted from a copy kindly sent to us.

and lastly the separation takes place of the d-benzaldehyde cyanohydrin from the optically active complex. The mandelic acid which was produced by the saponification of the nitrile was shown by its constants (m. p. 133 to 134°; $[\alpha]_D$ — 153,78°) to be polarimetrically pure. Optically active nitriles could also be obtained from anisic aldehyde and cinnamic aldehyde. Enzymes which, in addition to a catalytic action (such as was also found to exist in the case under review), possess a "directing" action, such as had not been observed hitherto, are called by Rosenthaler "asymmetrases". The author is of opinion that such cases as that described by him afford data for an understanding of the process of asymmetric syntheses in plant-cells.

With regard to a method for the colorimetric determination of benzaldehyde in extracts of bitter almonds, see Analytical Notes.

Aloe wood Oils. Moszkowski[1]) has published a few short notes on the subject of the Javanese scented wood *Kaju garu* (*Kaju gaharu* = eagle wood) which we described in our last Report[2]). He has found in Sumatra the tree which yields the "eagle wood", and which is locally known as *Karas*, and describes it as a fine tree, often reaching a height of 40 meters, with a smooth, grey bark and a splendid umbrageous crown. In general, his statements with regard to the wood and the method by which it is obtained agree with those of Boorsma[3]). On the other hand, Gilg, who examined a branch without blossoms or fruit gathered by Moszkowski, classifies the plant botanically as a new species of aquilaria (*Aquilaria Moszkowskii*) which is stated to be most nearly allied to *Aquilaria malaccensis* Lam. and *Aquilaria grandiflora* (Lour.) Gilg, whereas according to Boorsma the *Kaju garu* of Java is derived from *Gonystylus Miquelianus* T. et B.

Andropogon Oils. As a result of a communication in the last Buitenzorg Annual Report[4]), we are able to amplify a note in our last Report on the subject of the oil of an unknown variety of Andropogon which had been examined at the Buitenzorg Botanical Institute[5]), by stating that the oil in question contained geraniol to the extent of 18,7 % esterified, and 30,1 % free, geraniol.

Furthermore, an oil of *Andropogon intermedius* has been examined in the said Institute[6]). This oil had a specific gravity of 0,889 (26°) and an optical rotation α_D — 21° 52′.

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[1]) Notizblatt des kgl. botan. Gartens und Museums zu Berlin-Dahlem, No. 43 (Vol. V.), 8 and 83.

[2]) Report November 1908, 19.

[3]) Ibidem.

[4]) Report November 1908, 72.

[5]) Jaarboek van het Departement van Landbouw in Nederlandsch-Indië 1907, 67. Batavia 1908.

[6]) Ibidem.

From a new, likewise unknown Andropogon variety[1]) an oil was obtained at Buitenzorg with a lævorotatory power of 4° 8′, lack of material preventing the determination of further constants.

Possibly the last-named oil may have originated from the same plant of which Dr. de Jong, of Buitenzorg, kindly sent us a small sample of oil, with the observation that it had been obtained from a yet unknown variety of Andropogon. In order to distinguish this one from that previously referred to[2]) we will designate it as "Andropogon variety no. 2". This oil was pale yellow and had a peculiar odour, reminding at the same time of fatty aldehydes and of geraniol or methylheptenone; $d_{15°}$ 0,9961; α_D — 2°; $n_{D20°}$ 1,51236; acid no. 3,6; ester no. 7,3; soluble in 1 vol. of 80 per cent. alcohol; when 3 vols. are added the sample becomes cloudy. The oil reacted with bisulphite of sodium, and the product of reaction, when decomposed with carbonate of soda solution, yielded a fatty aldehyde which is possibly identical with decylic aldehyde, but which could not be examined in detail on account of the insufficiency of the material available.

Angelica Oils. In October last, as we reported at the time, the moment when the newly-distilled oil would be available was looked for with much impatience, and everywhere high prices had to be paid. Naturally, growers in Thuringia took advantage of the favourable position of the market for angelica root, and as a result of the strong competition it was difficult to obtain supplies. Our own cultivations have yielded an excellent material, and have enabled us to complete our supplies with a distillate of exquisite quality. The prices of pure angelica root oil ranged at first from 90 to 95 marks per kilo, but gradually advanced to 140 marks, and are still threatening to increase further. This movement of prices indicates that in all probability we are approaching a similar, if not still more severe, scarcity as that which prevailed last year, and that this season, too, far less oil will be produced than is required. Angelica seed was so dear that we did not feel inclined to risk distilling it, and for this reason we are not quoting angelica seed oil in our price list. Fortunately the demand for this article was so insignificant that its absence was not followed by any inconvenience.

Anise Oil. The comparatively low prices of the previous autumn, which enabled us again to take up the distillation of Russian aniseed, unfortunately did not last long, and we were therefore unable to secure even an approximately sufficient supply for our requirements. The aniseed market gradually advanced by 6 to 7 marks per 100 kilos, because a strong demand for export, especially to France, was ex-

[1]) Ibidem.

[2]) Report November 1908, 72.

perienced in Russia. The consumption of Russian oil of anise has of course decreased very considerably since anethol, which was first brought into commerce by us, has not only established itself in the manufacture of liqueurs, but has also been introduced in almost all modern Pharmacopœias.

Oil of Artemisia lavandulæfolia. The oil of *Artemisia lavandulæfolia,* a plant growing wild in the Tengger Mountains (Java), has been examined by the Botanical Institute at Buitenzorg.[1]) It had $d_{26°}$ 0,924 and rotation α_D — 7° 32′. On cooling, the bulk of it solidified and the crystals which separated out in the congealing process appear to possess the molecular formula $C_{12}H_{14}O_2$, but owing to the lack of sufficient experimental material it was impossible to determine the structure of the compound.

Basil Oil. From the South of France we received two light brown distillates, from the species known there as *Basilic nain* or *petit basilic* (*Ocimum minimum* L.) which agree as to their constants with the current commercial oils of German and French basil from *Grand basilic* (*Ocimum basilicum* L.), while differing markedly from the latter in their peculiar aromatic odour and their chemical composition. The two distillates in question contain about 14 % of eugenol, which was identified by its benzoyl compound (m. p. 69°). Linalool also appears to be present, at least the phenol-free portions of the oil had a distinct linalool odour. Whether the specimens also contain methylchavicol, the principal constituent of the oils of commerce, we were unable to determine, because the samples at our disposal were too small. For this reason, too, our examination was necessarily almost limited to the ascertainment of the general constants: —

	$d_{15°}$	α_D	Acid no.	Ester no.	Phenol cont.	Solubility in 80 p. c. alc.	Solubility in 70 p. c. alc.
1.	0,9102	— 11° 58′	5,3	12,5	14 %	in 0,6 vol. and more	in 2 vol. with 10 vol. opal.
2.	0,8901	— 13° 36′				in 1 vol. and more	in 2,5 vol., from 4,5 vol. upwards cloudiness.

Bay Oil. The sale of this article is becoming slower and slower, but as within the past few years the output in the West Indies of cheap bay oil, mostly of doubtful quality, has decreased to a large extent, there is no prospect of any over-production, and prices can be maintained at their present level. It is a pity that so very little interest is shown nowadays for that refreshing article, Bay rum.

[1]) Jaarboek van het Departement van Landbouw in Nederlandsch-Indië **1907**, 66. Batavia 1908.

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Fr. Watts and H. A. Tempany[1]), of Antigua, have made researches into the question in how far the age of bay leaves affects its yield of oil and the properties of the oil produced. With this end in view they distilled both young and old bay leaves from Montserrat. The values which were ascertained were of such a character that it is impossible to draw any direct inferences from them.

	Oil yield	Sp. gr. of the oil	Phenol content
Young bay leaves . . .	1,27 %	$d_{15°}$ 0,9648, $d^{30°}_{15°}$ 0,9507	60 %
Old bay leaves	1,50 %	„ 0,9612, „ 0,9480	61 %
Young bay leaves . . .	1,12 %	— $d^{28°}_{16,6°}$ 0,9308	53 %
Old bay leaves	1,10 %	— „ 0,9505	60,5 %

It is also worthy of note that, contrary to previous statements in the *West Indian Bulletin*, according to which *Pimenta acris* was said not to flourish in the limestone soil of Antigua, Watts and Tempany report that a considerable number of these trees are found in the island.

Lemon-scented Bay Oil. Whereas the genuine bay leaves are derived from *Pimenta acris* Wight, Watts and Tempany[2]) state that a variety known as *Pimenta acris* var. *citrifolia* occurs in the West Indian Islands which externally resembles the genuine bay tree, but which yields an oil known as "lemon-scented bay oil" on account of the fact that its odour reminds at the same time of bay and of lemon. Both these varieties of *Pimenta* are found growing side by side in the Islands of Dominica, Montserrat, Barbuda, and Antigua. Fishlock has made other investigations with regard to the distribution of the trees in the Virgin Island of St. John, where the genuine bay tree predominates, whereas in Tortola almost exclusively the *citrifolia* variety grows.

Up to the present little is known concerning lemon-scented bay oil. An oil of this kind distilled many years ago by J. H. Hart possessed, according to our determinations, a specific gravity of 0,882 (25°) and an optical rotation of — 0° 37′. The presence of citral was shown by the preparation of α-citryl-β-naphthocinchonic acid[3]). The citral content afterwards determined by Watts and Tempany by the bisulphite process was 65 %. The last-named authors have lately prepared a similar oil themselves from leaves grown in the island of Tortola. They obtained a yield of 1,11 % of a pale yellow oil of a pronounced lemon-like odour with a peculiar additional aroma reminding

[1]) West Indian Bulletin **9** (1908), 273. From a copy kindly sent to us.
[2]) West Indian Bulletin **9** (1908), 275. From a copy kindly sent to us.
[3]) Report October **1896**, 73.

of cress: $d\frac{27°}{16,6°}$ 0,8937, α_D —0,16°, citral content 44 %, phenol content 10 %; the oil dissolved completely even in 60 per cent. alcohol. Unfortunately the volumetric proportion of solubility is not stated.

Calamus Oil, Javanese. A calamus oil distilled by Dr. Carthaus in Java has been examined at the Botanical Institute in Buitenzorg [1]). It possessed the following constants: $d_{26°}$ 1,06, α_D + 0° 52′, sap. no. 9.

We have had an opportunity of examining two calamus oils from the same source which behaved very similarly. They had a yellow colour and a faint calamus odour. The constants of the one were: $d_{15°}$ 1,0783, α_D + 0° 53′, $n_{D20°}$ 1,55043, ester no. 12; of the other: $d_{15°}$ 1,0771, α_D + 0° 51′, $n_{D20°}$ 1,55065. The oils here referred to differ from ordinary calamus oil in their greater specific gravity, their much lower rotation, and their higher index of refraction. In normal calamus oil these values range within the following limits: $d_{15°}$ 0,96 to 0,97, α_D + 9 to + 31°, $n_{D20°}$ about 1,506. Moreover, the Javanese oils are already soluble (with slight separation of paraffin) in 1 to 1,5 vol. of 70 per cent. alcohol, while ordinary calamus oil is only soluble in 90 per cent. alcohol (in almost every proportion).

Camphor Oil. There has been very little change in the tendency of the camphor oil market during the course of the past five months. The dull state of business, as well as the fact that the existence of important supplies tied the hands of those interested, caused a further reduction in the quotations, and even at the present moment holders in Japan are inclined to accept reduced offers. The shipments from Japan were quite insignificant, except as regards a few thousand cases which were exported to the United States. Within the past few weeks camphor has shown a somewhat more animated tendency, which is probably accounted for by the fact that, since prices have reached a lower level than has been known for a very long time, the competition of artificial camphor may be regarded as entirely removed. For the present we regard it as very little probable that this firmer tendency will also influence the camphor oil market, especially in view of the enormous quantities which must have accumulated in Japan.

Wit regard to camphor plantations in Ceylon, the American Vice-Consul W. C. Doyle [2]) reports that in 1907 the area under cultivation was increased from 142 to 1106 acres, and that for 1908 apparently a still greater increase was projected. As a result of these extensions a

[1]) Jaarboek van het Departement van Landbouw in Nederlandsch-Indië **1907**, 67. Batavia 1908.

[2]) Oil, Paint and Drug Reporter **74** (1908), No. 23, page 52.

perceptible contribution to the World's requirements in camphor was to be expected. The camphor tree does not flourish in the coast region, but it does well in the mountainous districts of the Island, at altitudes between 2 500 and 8 000 feet. The yield of camphor from a cultivated area of from 15 to 20000 acres is estimated at 8000000 lbs., which according to most authorities is the quantity needed to supply the World's requirements, and hopes are entertained in Ceylon that, within the course of a few years, more camphor will be produced in the Island than is consumed on the entire globe at the present time. Among planters, the rapid growth of the branches of the camphor trees is regarded as the cause of the pre-eminence of Ceylon over other camphor-producing countries. The cost of producing natural camphor in Ceylon is estimated to be considerably lower, weight for weight, than the cost of the American synthetic product from oil of turpentine. The first experiments of cultivation in Ceylon were made by the Government with Japanese camphor seed, and the mode of cultivation consists in allowing the tree to reach a height of 40 ft. (which it does in about $3^1/_2$ years), when it is cut down to 4 or 5 ft. With this object in view the trees are pruned every 4 and sometimes every 3 months. The trees are planted at distances of 4×8 ft., which gives 1360 trees to the acre. Experiments of distillation made with the wood cut from an acre of ground, produced 190 lbs. of camphor. One planter maintains that he has obtained a particularly high yield of camphor by pressing the branches instead of distilling them. But although he vouched for the truth of this statement, he refused to disclose any particulars as to the process.

The Official Customs Statistics indicate that in 1907 a parcel of camphor weighing 562 lbs. was exported from Ceylon, and it is inferred from this that the quantities to be exported annually in the future will increase in geometrical proportion.

An American expert, Prof. Hilgard[1]), has written on the subject of the question of the cultivation of camphor trees in the United States, his paper being a sequel to that of Rivière which was discussed by us at the time[2]) and which takes the same view. Prof. Hilgard has made enquiries from the experts in the Agricultural Department at Washington and in the Southern States of the U.S., as to the prospects of camphor cultivation. The first-named Authorities informed him that although the Government had made experiments in the growing of camphor trees in its Southern Experimental Stations, it doubted greatly in the financial success of such an undertaking, and for this reason it

[1]) Journ. d'Agriculture tropicale **8** (1908), 360.
[2]) Report November **1908**, 36.

does not supply camphor seed to any private people, who are able to obtain their requirements of such seed from the trees which had already previously been planted in Florida and California. In most of the plantations the trees are regarded only as ornamental, and are treated as such, but in some of them experiments have been made to obtain camphor by distilling the leaves, either with or without stalks. The results of these experiments are not reported by the author, who only deals with his own experiments in making industrial use of the Californian camphor tree. According to these experiments, mature green leaves yield about 1 per cent. by weight of camphor, and it is to be noted that leaves and green twigs contain more liquid oil and less solid camphor. Up to the present no higher yields of camphor have been obtained. Hilgard observes that he has experimented only with trees growing in the misty, cool climate of the coast, and not with trees from the warmer and higher altitudes, for instance those from the interior of California. Although the latter trees no doubt might promise a higher output, seeing that odoriferous plants such as jasmine, mignonette, and heliotrope also flourish in the interior of California, Hilgard refrained from making any far-going experiments, because of the excessively high wages (for the harvesting of the leaves), which in those districts are an obstacle in the way of the development of the camphor industry as well as of other industries. The author therefore agrees with Rivière that there is no question of any American industrial competition with the natural riches and low wages of the island of Formosa, particularly as just at the present time the prices for crude camphor are low and are likely to remain so.

With regard to the prospects of synthetic camphor, Hilgard is of opinion that any serious competition with the natural product is out of the question until there has been a considerable increase in the present moderate yield, which equals only 25% of the turpentine oil used. Moreover, account has to be taken of the quickly progressing exhaustion of the American turpentine forests. Hilgard conjures up a future vision of the preparation of camphor from petroleum, which is certainly a distant prospect and not a very credible one at the present time. At any rate, the experiments which have for their object the replacement of camphor by similar materials have much more chance of being realised.

In an appendix to the paper, Cayla lays stress upon the complete agreement of Hilgard with the views frequently expressed by him (Cayla), to which we have referred in previous Reports. Cayla regards Hilgard's statements as an indirect confirmation of the conclusions arrived at by Giglioli[1]), insofar as the latter particularly referred to the

[1]) Report November **1908**, 36.

lowness of the wages in Italy and the age of the Italian camphor trees. Cayla is of the same opinion as Beille and Lemaire[1]), and also Giglioli, that the camphor production of the future will be established on the basis of making use of the leaves, a process which is already being applied in Formosa and Ceylon. Cayla also calls special attention to the impossibility of synthetic camphor becoming a serious competitor, in view of the present state of the prices; but in regard to this aspect of the matter he thinks that a change might be brought about if coniferous trees yielding turpentine or a similar oil were cultivated in suitable countries, especially in India and in Tonquin.

Cayla[2]), in his review of Giglioli's book *La canfora italiana* (to which work reference has also been made in our Report[3])), points out, in opposition to Rivière[4]), that according to the experience of Giglioli it is not necessary to remove the newly-grown leaves from the tree, thereby checking its growth. According to Giglioli, a satisfactory yield of camphor may be obtained from the leaves which have been shed by the tree and have been dried naturally by exposure to the atmosphere, the loss caused by the drying process not being considerable. Artificial desiccation, on the other hand, may cause a loss of camphor-content up to 50 %. The suitability of dry leaves for distilling purposes is of interest, because this fact would appear to make it possible to press the leaves for transport to distilleries situated in suitable localities.

Watts and Tempany[5]) have prepared essential oil from the wood, leaves, and twigs of camphor trees grown in the botanical gardens in Dominica, with the following results: —

1. 90 lbs. wood yielded 7,1 fl. oz. of oil; $d\frac{27^\circ}{16,6^\circ}$ 0,9012, α_D — 13,1°.

2. 33 lbs. leaves and twigs yielded 2,75 fl. oz. of oil; $d\frac{27^\circ}{16,6^\circ}$ 0,9024, α_D — 18,4°.

3. 29 lbs. leaves and twigs yielded 6,2 fl. oz. of. oil; $d\frac{27^\circ}{16,6^\circ}$ 0,8987, α_D — 19°.

The low yield of oil in the second experiment is attributed by Watts and Tempany to the insufficiency of the condensing apparatus, which caused the loss of a considerable proportion of the oil. All the distillates were clear and colourless, and even during the cooling

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[1]) Report April **1908**, 21; November **1908**, 35.
[2]) Journ. d'Agriculture tropicale **9** (1909), 60.
[3]) Report November **1908**, 28.
[4]) Report November **1908**, 36.
[5]) West Indian Bulletin **9** (1908), 275. From a copy kindly sent to us.

no camphor separated from them, which shows that that substance cannot be present in any considerable quantities. Watts and Tempany also state that in his annual Report for 1906[1]), Consul Playfair pointed out that the occasional absence of camphor from the oil was ascribed by many theorists to the circumstance that only those camphor trees which grow near the coast attain their full development[2]), while others declare that male and female camphor-trees grow isolated and that only the former contain camphor. Playfair considers the last-named theory to be incorrect, as the flowers of *Cinnamomum* are polygamous.

Cananga oil. The firmness which characterised the past autumn has now given way to a certain dulness, due to larger supplies, increase of the consignments to European markets, and lack of desire for buying. We have thus been enabled to reduce our quotations somewhat.

From a report by A. W. K. de Jong[3]) referring to an official visit of inspection made by him to Serang, we take the following information on the production of cananga oil in Java: As the distilleries are at a distance from the plantations, the flowers have to be carted to them. The distilling apparatus into which the flowers (which have previously been pounded) are placed, consists of a copper boiler, fitted with a tube through which water may be poured during the process of distillation. The boiler is connected with the condenser by a copper helm. The copper cooling tube, which has a diameter of about 6″, is connected diagonally with a large earthenware pot containing the cooling water, which is not renewed by a constant inflow, but is only replenished when necessary. In the place of Florentine flasks, wine bottles are employed as receivers for the distilled oil. These bottles have a small hole in the kick and are placed in a copper basin filled with water in such a way that the neck of the bottle protrudes above the rim of the basin. The basin, in its turn, is placed on a earthen dish, in order to catch the water that flows over from the copper basin during the process of distillation. This water is returned to the still. Every parcel of flowers is continuously distilled for two days, and during the second day the cooling is only done imperfectly.

In Manila an ylang ylang oil is prepared from cananga flowers which is worth ten times as much as the oil prepared in Java from similar flowers, and it would therefore be desirable to ascertain whether the more valuable variety of oil could not also be obtained from the Java flowers by fractionation. The investigations which were set on

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[1]) Diplomatic and Consular Reports No. 3913, August **1907**.
[2]) Compare Report April **1908**, 23.
[3]) Teysmannia **1908**, 578. Batavia. From a copy kindly sent to us.

foot by de Jong[1]) with this object have been greatly facilitated by the information furnished by Bacon[2]). The latter has shown that most first-class Manila ylang ylang oils have a sap. no. of above 100, while the second grade, of which the value equals that of cananga oil, always has a sap. no. below 100. De Jong found that fractions of oils distilled in various factories at Serang possessed the following constants: —

Brand	α_D	Sap. no.	Sap. no. after acetylation
A.	— 23° 0′	27,1	76,7
B.	— 28° 30′	24,1	77,8
1.	— 24° 10′	29,1	—
2.	— 29° 45′	33,0	—
3.	— 35° 0′	32,6	—

As the ester and alcohol content of these fractions was much lower than that of the ylang ylang oil itself (which may possibly be due to the insufficient cooling during distillation), de Jong distilled some flowers himself, which he obtained from the neighbourhood of Tjibinveng and Tjiterep, near Depok. Partly green and immature flowers yielded the following fractions: —

1. α_D — 21° 32′; sap. no. 17,5
2. α_D — 39° ; sap. no. 23,8
3. α_D — 35° 40′; sap. no. 23,0

Red, over-mature flowers also, either distilled whole or after being pounded, produced only fractions with a rotatory power ranging between α_D — 12° 56′ and α_D — 35° 0′, and a sap. no. between 9 and 17.

Oil from Batavia flowers gave fractions of α_D — 20° 37′ to — 38° 0′ and sap. no. 33,6 to 37,3. This oil is better than that from the Depok district, and resembles rather the product obtained in Serang.

According to de Jong, the difference in the constitution of the oil depends upon the site of the trees and upon climatic conditions, but it may also be due to minor botanical differences in the trees. Efforts are to be made to obtain seed and seedlings of *Cananga odorata* from the Philippines, and to acclimatise them in Java, in order that the causes of the difference in the constitution of the Philippine and Java oils may hereafter be made clear.

De Jong further lays special stress upon the fact that the volatility of the esters contained in the oils under examination is not greater than that of their other constituents, because the sapon. numbers of the successive fractions show very little variation.

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[1]) Milit. Tijdschrift **1908**, 1. Batavia. From a copy kindly sent to us.
[2]) Comp. Report November **1908**, 128.

We wish to be allowed to offer a few comments upon the interesting researches of the esteemed author: —

Chemically, cananga oil and ylang ylang oil differ in that cananga oil contains fewer esters, fewer alcohols, and more sesquiterpene. According to de Jong, this is due chiefly to the influence of climatic conditions upon the cananga trees. In Java also there are trees of which the flowers have a somewhat different and more agreeable odour, and de Jong was able to obtain flowers from these trees, which are known as *Canangadedes*. From these flowers he obtained an oil of a somewhat higher ester content, but the ester content of ylang ylang oil could not even approximately be reached, because he did not change the distilling process but carried out this distillation also by means of water.

It is possible that climatic conditions have something to do with the matter, but in all probability the mode of manufacture is of greater importance as regards the difference in the two oils. In any case it may be taken for granted that the distillation process followed in Java must result in an oil poor in esters and rich in sesquiterpenes. This is another example of the great differences which may exist in the character of essential oils according to the method of distillation by which they were obtained.

In the first place, flowers used for distilling purposes should never be pounded. There are not many flowers in which such a process can be applied without injuring the quality of the essential oil. In the case of fleshy, juicy flowers, the pounding process may easily give to the oil an additional herbaceous odour. It is true that by pounding the flowers distillation is facilitated and that the yield of oil is increased, but in this particular case it is at the expense of the perfume of the oil. The destruction of the flowers liberates the essential oil from the cellular tissues, and thereby enables those constituents of the oil which are insoluble in water and have a high b. p. — among them especially sesquiterpene — to volatilise more easily, while volatilisation of such constituents from entire flowers is difficult and only possible to a very slight extent. This explains the higher proportion of sesquiterpenes with a high b. p. in cananga oil.

Distillation by water in the case of this oil is also a mistake, because it has a decomposing action upon the esters and because it impedes the evaporation of those parts of the oil which are the most readily soluble in water, especially of benzyl alcohol and of isoeugenol

The decomposition of the esters is further increased by the long duration of the distilling process, for it is impossible to distil rapidly owing to the totally insufficient means of cooling.

Again, the distillation water should not be returned to the flowers, as it contains acetic acid from the destroyed esters, and, according

to Bacon, also perhaps formic acid, which have an even more decomposing action upon esters than boiling water. Distillation water, which is rich in oil, should be distilled by itself, and all the water which has evaporated from the still should be replaced by pure water. Finally, owing to the weak distillation, the mass of distilling material in the still will generate steam without being thoroughly stirred up and kept in motion. Hence it is probable that parts of the flowers will adhere to the bottom of the still kept hot by the fire, and will burn to it, which would impart to the oil a sharp and more or less acrid odour.

It is very probable that it would be possible to obtain ylang ylang oil from cananga flowers in Java if the flowers were not crushed, and if, instead of water distillation, distillation by water-and-steam were applied; in the manner, for instance, in which the Chinese distil the camphor wood in Formosa and the Siamese the fruit of star anise in Tonquin. In such cases quick distillation and consequently an efficient cooling apparatus are necessary; the distillation of one charge of the still should not take more than a few hours.

The principle of distillation by water-and-steam is that the charge in the still rests upon a perforated bottom, between which and the bottom of the still there is water, which is separated from the charge itself by a space in which steam can circulate. The water may be brought to boiling either by heating with fire, or by a closed steam-worm. By means of a tube at the bottom of the still the evaporated water is replaced by pure water during the process of distillation. The quantity of the water of distillation which is collected is a certain indication as to when and how much water should be added to the still. At the end of every distillation the still should be emptied of water.

Prof. Preuss[1]) reports that experimental distillations of the flowers of *Cananga odorata* made in New Guinea have yielded highly satisfactory results. The flowers gave 0,98 % of oil and there is a prospect that the oil production will increase. A cananga oil which has been sent to us from New Guinea for examination, showed the following constants: $d_{15°}$ 0,9143, α_D — 21° 20′, ester no. 24,1; soluble in half its vol. of 95 per cent. alcohol; when the solution is diluted with alcohol of the same strength it becomes turbid.

Caraway Oil. For the present the reports from the producing-districts in Holland agree that the prolonged winter has in no way damaged the plants, but has only retarded their growth, with the result that they promise to develop all the stronger and more vigorous

[1]) Berichte d. deutsch. pharm. Ges. **19** (1909), 25.

for the delay. No definite information is yet available as to the extension of the area devoted to caraway-growing, but it is reported that, as compared with 1908, more has been planted in Brabant, Flanders and Zealand, considerably more in Groningen, and one-third more in North Holland. Many farmers are said to have put the whole of their land under caraway. This considerable extension of the area under cultivation is probably to be ascribed to the good prices which were realised last season. The only stocks of caraway are now in the hands of the exporters, and an important decline in the price is all the more improbable for the present because the existing supplies may hardly last until the new crop is on the market. New season's seed for August/September delivery is being offered for the present at about 25 % less than seed for immediate delivery. So far, therefore, the prospects are favourable, and if the anticipations are not dashed to the ground by bad weather in the spring and summer, low caraway oil prices are to be expected next autumn. Until then the market will probably remain approximately as it is now.

Cassia Oil. The expectations expressed in our last Report have even been exceeded by the changes in prices of the article, inasmuch as the quotations for 80 to 85 per cent. oil have since then receded to 3/5, probably in the first place under the pressure of the low rate of exchange for silver. Even at the present time, owing to want of demand, the market wears a thoroughly lifeless aspect, so that we think we are justified in prophesying a further reduction in value.

Oil of Cassie Blossoms. On the subject of the occurrence and cultivation of the two varieties of acacia which yield the oil of cassie flowers, viz., *Acacia Farnesiana* Willd. and *A. Cavenia* Hook. et Arn., we abstract the following particulars from an article by L. Mazuyer[1]). The original habitat of the cassie shrub is India, but it is also a native of Angola, Australia, the Sandwich Islands and the Philippines[2]). It has been introduced by cultivation into Italy, France, Algeria, Egypt and Syria, and the name *Farnesiana* is said to have been derived from the fact that the plant was first grown in the gardens of Farnese. Both varieties of acacia are found in Provence, in France. The flowers of *A. Farnesiana*, known in commerce as *Cassie Ancienne*, have a finer odour and are more expensive (about fr. 5 to 6 per kilo) than those of *A. Cavenia* (about fr. 2 to 3 per kilo). The usual trade name of the latter variety, *Cassie Romaine*, is probably traceable to its having been brought from Italy to Cannes about a century ago. *A. Cavenia* has the advantage of being less

[1]) Journ. de la Parfumerie et Savonnerie **21** (1908), 254.

[2]) With regard to its occurrence in other places (Cuba, New Caledonia, and the Congo State), see our Reports April **1905**, 21; April **1907**, 27.

sensitive and requiring less care than *A. Farnesiana*, the latter needing careful pruning every year in March, which is not at all necessary in the case of the other plant. Both varieties like a light, sandy granite soil, but they require a warm and sunny situation, protected against the wind, especially the *Mistral*. The mode of cultivation differs, *A. Farnesiana* being raised from seed, *A. Cavenia* from cuttings. In both cases the planting takes place in March. As soon as the plants have struck sufficient root, they are planted out, *A. Farnesiana* at distances of from 2 to 2,5 m., *A. Cavenia* at from 5 to 6 m. Occasionally, *A. Cavenia* is grafted upon *A. Farnesiana*. The plants demand very little manure, and many farmers fertilise them only every other year. The soil also requires little watering, but this must not be onitted altogether.

The cassie shrubs flower in the first summer after their planting-out, but a full crop can only be looked for from the 5th year onwards. The flowering time of *A. Farnesiana* is from September until the end of December, a medium-sized shrub producing during that time about 600 g. of flowers. *A. Cavenia* flowers considerably longer, that is to say, until April or May, and its yield of flowers is frequently more than double that of the quantity above mentioned. The *Cavenia* flowers are frequently used to adulterate the others, which is all the more easily done as they are difficult to distinguish from the flowers of *A. Farnesiana*. We have given detailed information concerning both oils in previous Reports [1]).

Chamomile Oil, Roman. H. J. Henderson [2]) has observed from authentic distillates of *Anthemis nobilis* that, contrary to what is generally stated, the rotation does not lie between + 1 and + 3°. Three oils, distilled from dry flower heads, were inactive, while of two oils obtained from the entire, green plant, one was inactive, while the other had a dextrorotatory power of 0° 30′. In the case of the last two oils referred to the sap. no. was 283 and 297 respectively, while for the first-named three oils it was respectively 305, 307 and 317, that is to say, higher than has up to the present been indicated for Roman chamomile oil (250 to 300). The acid number of freshly distilled oils ranged up to 4, in the case of a four-year-old oil it was 7,8. This old oil was also less soluble than the fresh distillates, all of which gave a clear solution with 6 vol. of 70 per cent alcohol. Henderson also questions Gildemeister's and Hoffmann's statement that the Roman chamomile grows wild only in a few districts of Western Europe [3]). According to him the Roman chamo-

[1]) Reports April **1901**, 18; April **1903**, 17; October **1903**, 18; April **1904**, 23; October **1904**, 18; April **1907**, 27.

[2]) Pharmaceutical Journal **81** (1908), 683.

[3]) Gildemeister and Hoffmann, *The Volatile Oils*, p. 672.

mile is a specifically British plant and, in the wild state, is known as Scottish chamomile. This is, however, incorrect, as the Roman chamomile occurs wild in France, also in Southern Europe, particularly in Italy (hence the name of Roman chamomile), and in Spain.

We may add furthermore to the above statements that we also have frequently examined Roman chamomile oils of the best quality with a rotation below + 1°; these, however, were very rarely inactive, but this point cannot always be determined because of the colour, which is often very dark. The acid numbers found by us lay between 1,5 and 3,5, the saponification numbers between 250 and 300. From 6 to 10 vols. of 70 per cent. alcohol were required to bring about solution, cloudiness occasionally ensueing; all the oils gave clear solutions with 1 to 2 vols. of 80 pei cent. alcohol.

Cinnamon Oil, Ceylon. We continue, as before, to devote special interest to the distillation of this important article, and we are able to state with satisfaction that owing to the exquisite quality of our product our sale has experienced a considerable increase. The prices of pure cinnamon oil remain unchanged, and the market for the raw material also has shown but slight fluctuations. The exports of Ceylon cinnamon chips were as follows: —

in 1908	2785824	lbs.
„ 1907	2835936	„
„ 1906	2531614	„
„ 1905	2325514	„

Of this total, Hamburg imported: —

in 1908	about 554400	lbs.
„ 1907	„ 473200	„
„ 1906	„ 386400	„

Our own consumption in the past year reached about 115000 kilos, that is to say, approximately about one-half of the total quantity imported via Hamburg.

It is remarkable that in 1908, 200878 ounces of cinnamon oil distilled in Ceylon were exported, a figure reached never before, of which over one-half went to England. Compared with 1907, these figures indicate an increase in the exports of over 100 %, and the fact that, this notwithstanding, our distillate found a ready sale at full prices, should afford sufficient proof of its superiority.

In considering the export figures of Ceylon oil given above, it should be remembered that within the past year large quantities of cinnamon leaf oil were shipped from Ceylon, and that these are included in the above statistics. The manufacture of the last-named article has been carried on with an intensity that can only be characterised as senseless, no regard having been paid to the very limited consumption.

In an article in *Southall's Report*[1]) the just desire is expressed that the Pharmacopœia requirements relating to Ceylon cinnamon oil should be extended so as to include a definite aldehyde content, in order to prevent adulteration by means of artificial cinnamic aldehyde. The cinnamic aldehyde content of normal oils has been ascertained to range between 70 to 71,4 % whereas adulterated oils have been found to contain from 77,6 to 86,4 %. The specific gravity of normal oils moves between 1,012 and 1,023, in adulterated oils it ran from 1,027 up to 1,055.

The observations relating to the specific gravity of alleged authentic oils recorded in this article do not agree with our own findings, which are the result of records of very numerous observations with our own distillates. We have found the specific gravity of normal Ceylon cinnamon oils to vary from 1,023 to 1,040; lower specific gravities may perhaps be due to the use of defective raw material or to unreasonable methods of distillation. According to our experience, the aldehyde content of good Ceylon cinnamon oils ranges from 65 to 76 %.

Cinnamon bark Oil, Seychelles. In completion of what we wrote in our last Report[2]) with regard to the Seychelles cinnamon oils, we may state that cinnamon trees growing in the Seychelles Islands are said to be originally deriving from Ceylon. It is stated that an inhabitant of the Seychelles brought over a number of young plants from Ceylon. No further trouble was taken with these, yet they flourished greatly and finally began to spread luxuriantly throughout the islands. The trees develop and are replenished very quickly and were used on the Seychelles hitherto merely as fuel. From this it may be surmised that the Seychelles cinnamon tree represents its Ceylon congener in the wild state. This view is confirmed by an article on the oil industry in the Seychelles in the *British and Colonial Druggist*[3]), from which we quote the following particulars concerning the occurrence and distillation of cinnamon. Cinnamon trees have been growing in the Seychelles for about a century, the seed having been carried thither by birds. In Mahé the trees are found from the highest mountain-districts down to the coast. Occasionally, especially on the borders of the streams, the plant attains enormous dimensions. Fine trees of about one foot diameter produce about 100 lbs. of dry bark, but the smaller plants may also be used for chips. In Ceylon the bark, after having been freed from the epidermis by scraping, is left to ferment overnight in damp sacks, then dried in the shade

[1]) Southall's Report **1908**, 17. Quoted from Year-Book of Pharmacy **1908**, 53.
[2]) Report November **1908**, 41.
[3]) British and Colonial Druggist **54** (1908), 152.

for two days and finally exposed to the morning sun on two days. In the Seychelles less time and labour are applied to the work. Here it is thought sufficient to leave the unscraped bark of large trees to dry in the sun for three or four days, as experience has proved that the scraping makes no difference to the yield. Experiments with green, half-dried and fully-dried bark have shown that the dried bark gives twice as much oil as does the green, but that the loss in weight during drying is almost in proportion. On the other hand, the oil from the dried bark has a more agreeable odour and a less acrid taste than that from the green. It is said that in January 1908 the oil yield amounted to 9,4 and 9,2 % respectively of the raw material[1]). The yield depends upon the season; increasing in March, when the leaves begin to form, and probably continuing to increase from May up to September. Towards the end of the year, under the influence of the rainy season, it attains its maximum. Similar experience has been gained in Ceylon, where the preparation of the bark is begun about three weeks after the setting-in of the rainy season in May or November. As already stated, large plants yield about 100 lbs. of dry bark, but the average yield is only about 20 lbs., not counting the small branches, which contain an equal proportion of oil. At the present time only the wild-growing plant is used, but perhaps the seed may be sown in districts which are unsuitable for more remunerative cultivation. This will have to be done if more factories should be built, as in that case the material available for distillation would be insufficient. Up to the present only one works of this kind is in existence. This has been built in Sans-Souci and has a steam-boiler and a still with a capacity of 4000 liters. The stills formerly used for experimental distillations were only one-quarter that size.

Besides the bark, the leaves have also been distilled for experiments' sake, but their oil has been found to be less valuable than that of the bark. On the other hand, root-oils have not yet been prepared, as the trees are only cut down and not grubbed up.

The hopes which are built upon the pecuniary profit to be derived from the industry appear to us to be exaggerated, if it is thought possible to compete with the cinnamon oils distilled in Europe from Ceylon chips. According to the experience which we have made so far, the quality of the Seychelles oils is very much inferior to that of the former.

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[1]) Such a high yield would be unique. The best Ceylon cinnamon yields about 1 %, and Seychelles cinnamon is not likely to yield about ten times as much. No doubt the statements made above are due to a printer's error: it was probably intended to read "0,94 and 0,92 %" respectively.

Cinnamon root Oil. A. A. Pilgrim[1]) has examined the oil obtained from the green root-bark of *Cinnamomum zeylanicum* Breyne by means of distillation with steam. The oil was a pale yellow liquid, with a strong odour of camphor, while camphor was found separating out of it at ordinary temperature. The following constants were determined: $d_{15°}$ 0,99366 and α_D + 50,2° (?). The constituents of which the presence was determined were: pinene, dipentene, phellandrene, cineol, camphor, eugenol, safrol, caryophyllene and borneol. We may remark on this that the separation of camphor has long been known, and that Holmes[2]), many years ago, showed that the oil also contains cinnamic aldehyde.

Citronella Oil. As was to be foreseen, the prices of this article have moved in very narrow limits; nominally they remain below 1/- cif. even at the present time, although exporters in Ceylon until quite recently stood out for somewhat higher rates.

The exports from Ceylon amounted to 1276965 lbs. in 1908
against 1230159 „ „ 1907
„ 1107655 „ „ 1906
„ 1282471 „ „ 1905

The exports from 1st Jan. to 15th Feb. 1909 amounted to 126038 lbs.
do. do. 1908 „ 76291 „
do. do. 1907 „ 47041 „
do. do. 1906 „ 116017 „

The above figures show that the excess of exports in the first five or six weeks of the new year is already about 50000 lbs. as compared with the year before, from which it may be concluded that the reports as to scarcity of supplies which periodically reach us from Ceylon are not to be taken very seriously.

At the present time it is difficult to judge what course prices will take within the near future. Although on the one hand the increased exports may give rise to the belief that the consumption of this oil is again on the increase, we have on the other hand to take account of the fact that, because of the severe competition which exists among them, large soap manufacturers, especially in England, no longer consume anything like as large a quantity of citronella oil as in former years. Almost everywhere, slightly scented household soap is being superseded by strongly perfumed cheap toilet soaps — a result of the extremely low-priced synthetic perfumes which in recent times have found more and more favour with the public.

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[1]) Pharm. Weekblad **46** (1909), 50. Quoted from Chem. Zentralbl. **1909**, I. 534.
[2]) Pharmaceutical Journal **20** (1890), 749. Compare Gildemeister and Hoffmann, *The Volatile Oils*, p. 382.

In these circumstances, we believe that it may be assumed with some certainty that the present prices will not show any serious fluctuation for some months to come. There is absolutely no ground for expecting an advance in prices.

The sale of the highly popular Java citronella oil within the past few months has also been extremely sluggish, and indications are already perceptible of over-production, on the ground of which a prospective decline in prices of this variety is also to be looked for.

As in the case of lemongrass[1]), de Jong[2]) has also conducted experiments on the oil content of the various parts of Java citronella grass (*Andropogon Nardus* Java; *sereh wangi*) in different stages of development, in order to discover which is the most favourable time for distilling. The result was exactly the same as in the case of lemongrass; as the leaf ages the oil content decreases; the sheaths of the leaves and the roots contain much less oil than the leaves themselves. In this case also, de Jong considers it the best plan to cut the grass as soon as four or five leaves have developed. The greater richness in oil of citronella grass as compared with lemongrass was remarkable; the former usually yielded three or four times as much oil as did the latter. As regards the properties of oil from different batches of old leaves, the optical rotation and total geraniol content (= geraniol + citronellal) show only insignificant variations. The rotation varies irregularly; values ranging from $-2^\circ 7'$ to $-7^\circ 36'$ being observed in oil from leaves of various ages. The total geraniol content first increases in an ascending scale from the newest up to the oldest leaf and afterwards decreases in a corresponding manner; the lowest value was 85,5 %, the highest 93,3 %. The results of this investigation induced de Jong to make experiments as to the time required for acetylation, the behaviour of the oil towards acetic anhydride, the volume of acetate of sodium to be added, and the time required for saponification. On the basis of these enquiries de Jong considers that two hours are needed both for acetylation and for saponification, and that for every 20 cc. of oil and acetic anhydride, 2 g. of sodium acetate are required in order to produce accurate results. He concludes this because in his experiments on citronella oils, he obtained the best values by following this method.

The oils examined by de Jong were soluble in three parts of 80 per cent. alcohol; when more than four parts of the solvent were used, turbidity ensued. According to our observations, the Java oils of commerce make a clear solution with 1 to 2 vols. of 80 per cent.

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[1]) See Report November **1908**, 81.

[2]) Teysmannia, **1908**. From a copy kindly sent to us.

alcohol and more. Only in exceptional cases does the diluted solution show opalescence.

In our last April Report[1]) we called attention to the occurrence of dextrorotatory citronella oils, a phenomenon which had never previously been observed. An oil of this kind is also referred to in the Buitenzorg Annual Report for 1907[2]). It had an optical rotation of $+ 0°45'$ and a specific gravity of 0,87.

The experimental cultivation of citronella grass in the German Pacific Islands having been crowned with success, and resulted in the production of oils of good quality, closely approximating Java oil, we now gather from a paper read in Berlin by Prof. Preuss[3]) that *Andropogon Nardus* (author?) is to be more extensively cultivated, as its distillation has already been taken up on a large scale. From a specimen sent for our examination we have been able to satisfy ourselves of the good quality of the sample distillates. The specimen examined has the following characteristics: $d_{15°}$ 0,8819, α_D $-0°46'$, $n_{D\,20°}$ 1,46278; joint content of geraniol and citronellal 85,9%, soluble in 1,3 vols. and more of 80 per cent. alcohol.

Clove Oil. In concordance with the general condition of business, the sales of this important article dragged greatly, and remained restricted within the limits of a moderate turnover for consumption. No factors of any kind were present which might have induced to speculative undertakings, and thus all influence upon the clove market on the part of our industry was wanting. Particularly severe price-cutting in clove oil was again to be observed in London, but this "privilege" of our English colleagues is so generally known that we do not feel called upon to refer to it again at length on this occasion. It is not surprising that these cheap "clove oils" should sometimes exhibit remarkable properties.

As is our custom in our April Report, we will begin by reproducing the information supplied by the German Consulate at Zanzibar: —

Clove exports from Zanzibar in 1907.

The exports of cloves from Zanzibar were as follows: —

	Weight in pounds	Value in rupees
1904	14502775	4986449
1905	15312952	4306090
1906	15105760	5349545
1907	18214668	5941817

The exports of cloves in 1907 amounted to 39% of the total exports.

[1]) Report April **1908**, 32.

[2]) Jaarboek van het Departement van Landbouw in Nederlandsch-Indië **1907**, 67. Batavia 1908.

[3]) Berichte d. deutsch. pharm. Ges. **19** (1909), 25.

The exports were shipped to: —

	1904	1905	1906	1907
		Weight in pounds		
Europe . .	7312375	5673319	8939789	10457830
America . .	2056175	1769860	717909	1102420
Asia . . .	4839524	7810508	5355875	6553453
Africa . . .	94701	59265	92196	100965
		Value in rupees		
Europe . .	2633787	1676468	3176924	3387448
America . .	713420	401027	238975	306061
Asia . . .	1601061	2123255	1901368	2215262
Africa . . .	38191	15340	32278	33046

The shipments to the European markets were distributed as follows: —

	1905	1906	1907
	Weight in pounds		
Rotterdam . .	1814460	1543310	952006
London . . .	2762850	2650919	3298930
Hamburg . . .	633284	3841300	5529050
Marseilles . . .	218750	585760	418850
	1905	1906	1907
	Value in rupees		
Rotterdam . .	554887	557320	295300
London . . .	820638	915629	1112693
Hamburg . . .	181335	1387202	1770961
Marseilles . . .	54230	207338	125867

In addition to Europe, India absorbs a very large part of the clove-exports, viz.: —

1905	1906	1907
	Value in rupees	
1985878	1782609	2149154

The respective shares (in percentages) of the countries principally concerned in the trade are as follows: —

	1905	1906	1907
India	46,5	33,3	36,3
Germany	4,2	25,9	29,8
United Kingdom . . .	19,2	17,0	18,7
United States	11,5	5,4	5,1
Holland	13,0	10,0	4.9
France	1,0	3,8	2.1

In this connection it is to be noted, however, that the Customs Statistics indicate Germany as the country of destination of all cloves shipped in German vessels, whereas the B/L is mostly made out "option Rotterdam-London". London is the World's market for cloves, and the major part of the cloves alleged to be shipped to Germany does not go to Hamburg, but to London.

A table of the clove crops of the last ten years (each crop covers the twelvemonth from August to July) shows the following figures: —

Crop year	Island of Zanzibar	Island of Pemba	Total	Average price
		Frasilah[1])		Rupees
1897/98	44941	150703	195644	6.3.—
1898/99	149417	481505	630982	6.8.9
1899/1900 . . .	59751	206640	266381	6.1.—
1900/01	37567	201192	238759	7.—.—
1901/02	43626	321599	365225	6.6.6
1902/03	175420	251780	427200	6.8.6
1903/04	28369	96792	125161	13.4.—
1904/05	76860	675683	755543	9.5.6
1905/06	181536	109931	291467	11.14.3
1906/07	55833	202633	259466	13.—.—

Average yield of each crop: 355582 frasilah; average price of the last 10 crops: 8.9.3 rupees.

This price only applies to Pemba cloves; Zanzibar cloves are a little dearer.

No exact census has been taken of the clove-trees in the two islands, but from fairly reliable data it is estimated that, in round figures, there are 2000000 trees in Zanzibar and 3000000 in Pemba. The Government owns on its own plantations in Zanzibar about 130000 trees, in Pemba 26000 trees. Taking bearing and non-bearing trees together, one frasilah of cloves gathered represents the produce of 20,9 trees in Zanzibar, and, in round figures, of 10 trees in Pemba.

The last crop of the Government plantations yielded in round figures 7680 frasilah in Zanzibar and 4596 in Pemba.

The calculation of average yields is made extraordinarily difficult by the unusually heavy fluctuations in the output of the several plantations. A further factor in the uncertainty is that in years of an abundant crop, part of the trees cannot be picked at all on account of want of labourers.

Generally speaking, the want of sufficient labourers to harvest the clove crop has a disturbing effect upon the further development of this cultivation, and has driven the prices up to a considerable extent. Whereas, for example, the price formerly paid for gathering the cloves was 4 pesa per pishi (measure of capacity) of cloves, as much as 9 pesa had to be paid at the beginning of the last crop. Taking an average of 8 pesa, the wages paid for gathering come to $2^1/_2$ rupees per frasilah. About 20 pishi (= 50 to 60 lbs.) of green cloves equal one frasilah of dried cloves.

Last year about 1200 labourers from British East Africa were brought to Pemba by the Government, and it is reported that about 300 men came to Pemba from Zanzibar to gather cloves. In spite of this it is said to have been impossible to pick the whole of the crop.

The exports of clove stems amounted to: —

	1905	1906	1907
		Weight in lbs.	
Europe . . .	3777062	2317305	2055415
Asia	63835	63056	48125
America . . .	149426	—	179900
Africa	—	2065	—

[1]) 1 frasilah = 35 lbs. avoirdupois.

	1905	1906	1907
		Value in rupees	
Europe . . .	285818	222608	190197
Asia	3622	6831	4708
America . . .	9680	—	15060
Africa	—	285	—

As in the preceding season, almost the whole of the exports of the current year went to Hamburg, the value sent to that port being 175648 rupees out of a total of 209965 rupees.

The prices of cloves in Hamburg have shown a continued falling tendency since last October (when the highest point [108 marks] was reached), and when in the first half of February not less than 9500 bales were brought to market in Zanzibar, they dropped to 88 marks. In London and Amsterdam the quotations were for the time less advantageous, but these variations are fairly well counterbalanced by differences to the detriment of Hamburg at other times.

The estimate expressed in our November Report as to the yield of the clove crop in Zanzibar appears to have been taken too low rather than too high. It is now shown that the total production of the harvest will far exceed 90000 bales, inasmuch as the shipments already known of exceed 100000 bales. In well-informed circles a crop of, say, 130000 bales is even talked of, and although this figure may be put a little too high, because doubtless old stocks in warehouse have been counted in with the new crop, that fact in no way alters the decisive character of the total figures. The comparatively high prices of the past few months may therefore legitimately be put down to the usual manœuvring of the bull party, whose influence upon the course of the market is unmistakable even at the present time.

In the year 1908, in sympathy with the diminished demand, only about 767500 kilos of clove stems were imported via Hamburg,

compared with about 1200000 kilos in 1907
„ 850000 „ „ 1906
„ 1230000 „ „ 1905
„ 333000 „ „ 1904.

After slight movements upwards and downwards the prices receded from 32 marks per 100 kilos to about 27 marks to 28 marks per 100 kilos, but in the course of the past few weeks the market has shown a somewhat firmer tone.

From the residue of the distillation *in vacuo* of the sesquiterpenic parts of oil of clove stems (free from eugenol) E. Deussen[1]) has isolated about 0,1% of an amorphous body, unsoluble in alcohol and melting at about 146°, to which he ascribes the formula $(C_{21}H_{30}O)_5$.

[1]) Berl. Berichte **42** (1909), 380, 680.

Condurango bark Oil. In an exhaustive paper on the chemistry of condurango bark, K. Kubler[1]) also describes the essential oil which was obtained to the extent of 0,3 %, by subjecting the essential extract to distillation by water vapour. The oil is yellow and possesses an intense, not unpleasantly aromatic, slightly pungent odour, b. p. 140°(?), $d_{18°}$ 0,9741, $[\alpha]_D$ + 6,724°. By treating it with a 3 % soda solution he succeeded in isolating about 30 % of a neutral, pure constituent of pleasant aromatic odour (b. p. 225°; d 0,927; $[\alpha]_D$ + 19,56°) and an acid constituent, which congealed in crystalline form and consisted of a mixture of the higher fatty acids.

Copaiba Balsam Oil. E. J. Parry[2]) calls attention to the fact that many so-called copaiba oils are found in commerce at the present time which (although they conform to the requirements of the British Pharmacopœia), prove, when subjected to closer examination, to be merely a mixture of African copaiba balsam oil and of gurjun balsam oil, in suitable proportions. One such oil had the following constants: $d_{15°}$ 0,902, α_D — 14° 30′, soluble in 95 per cent. alcohol. It consisted almost entirely of sesquiterpenes. In acetic acid solution it gave with nitric acid the deep violet colour characteristic of gurjun balsam oil, and when it was fractionated, dextrorotatory portions were also obtained. It gave no crystalline compound with hydrochloric acid, but only an oil of a deep violet-blue colour.

Evans[3]) has examined a series of copaiba balsams of various origin, in the course of which he made certain observations on the oil content, rotation of the oil, and the acid no. of the residual resin after distillation by water vapour, which are set forth in the subjoined table:

	Oil content	α_D of the oil	Acid no. of the resin
Pará (Maranham) balsam	27 to 40 %	— 8° 40′ to — 17° 14′	124 to 150,4
Maracaibo balsam	35 to 46 %	— 2° 32′ to — 9° 50′	132,8 to 156
Carthagena balsam	56 %	— 16° 30′	151,8
	64 %	— 18°	143,4

Of 19 balsams under examination, one gave a faint gurjun balsam reaction, while two others probably contained small quantities of colophony.

Utz[4]) has published an article on the value of the various colour reactions in the determination of gurjun balsam in copaiba balsam.

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[1]) Arch. der Pharm. **246** (1908), 658.

[2]) Chemist and Druggist **74** (1909), 270.

[3]) Evans' Analyt. Report **1907**, 18. Quoted from Year-Book of Pharmacy **1908**, 58.

[4]) Chem. Rev. der Fett- und Harzind. **15** (1908), 218. Quoted from Chem. Zentralbl. **1908**, II. 1212.

According to him, most of these reactions are useless; only that of Dodge and Olcott, and Turner's test are said to yield unimpeachable results. According to Dodge and Olcott, 4 to 6 drops of concentrated nitric acid are added to a solution of 4 drops of copaiba balsam in 15 cc. of glacial acetic acid. Pure copaiba balsam remains unchanged; when gurjun balsam is present the glacial acetic acid solution becomes purple. In Turner's reaction, 3 to 4 drops of copaiba balsam are dissolved in 3 cc. of glacial acetic acid, a drop of freshly prepared 10 per cent. sodium nitrite solution is added to the solution and the latter is then very carefully poured upon 2 cc. of concentrated sulphuric acid. In the case of pure copaiba balsam the glacial acetic acid layer remains colourless, while if gurjun balsam is present, the solution gradually turns violet.

We made a control test of the two reactions referred to, and were able, on the whole, to corroborate the statements of Utz. But it must be noted that in Dodge's and Olcott's test the colour occasionally disappears very rapidly, while in the case of Turner's test the minutest care was necessary to carry out the overlaying of the sulphuric acid; otherwise the glacial acetic acid layer, instead of remaining colourless, turned brown very easily.

In connection with this matter we may point out that of the various balsams mentioned in our Report April 1905[1]) the Pará balsam, strange to say, gives the gurjun balsam reactions referred to above, so that it is scarcely doubtful that this balsam also was adulterated with gurjun balsam. As already mentioned by us at the time, these balsams had come to us at first hand, and therefore we had no reason at the time of doubting their genuineness, as in most cases adulterations are only resorted to by middlemen. In any case, the last thing that could be surmised was that in South America, the country of origin, gurjun balsam, which is an East Indian product, would have been added, for which reason even the high optical rotation of the balsam did not make us suspicious with regard to its quality. We therefore desire to take this opportunity of correcting our views as to the Pará balsam. We may again quote the constants which it was found to possess: $d_{15°}$ 0,9692, α_D — 41° 20′ acid no. 60,75, sap. no. (cold) 64,72. To water vapour it yielded 62,5 % of a yellow oil: $d_{15°}$ 0,9180, α_D — 78° 48′, acid no. 3,14, ester no. 0.

Coriander Oil. Plentiful supplies of this oil were available at unchanged prices; but, should the demand become brisker, it is probable that the quotation will have to be raised, as in that case the supplies will scarcely last until the next crop is available.

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[1]) Report April **1905**, 24.

Douglas fir Oil. The Douglas fir (red fir), which ranks among the most widely-distributed and valuable trees of North America and of the great coniferous forests in the North-Western United States, has the following botanical denominations: *Pseudotsuga mucronata* Sudworth, *P. Douglasii* Carrière, *P. Douglasii taxifolia* Carrière, *P. Douglasii denudata* Carrière, *P. Lindleyana* Carrière, *P. taxifolia* Britton, *P. Douglasii* var. *glauca* Mayr, *P. taxifolia* var. *elongata* Lemmon, *Pinus taxifolia* Lambert, *P. Douglasii* D. Don., *P. canadensis* B. Hooker, *P. Douglasii* var. *taxifolia* Antoine, *P. Douglasii* var. *brevibracteata* Antoine, *Abies taxifolia* Poiret, *A. mucronata* Rafinesque, *A. mucronata* var. *palustris* Rafinesque, *A. Douglasii* Lindley, *A. Douglasii* var. *taxifolia* Loudon, *Picea Douglasii* Link, *Picea Douglasii* Bertrand, *Tsuga Douglasii* Carrière, *T. Douglasii fastigeata* Carrière, *T. Lindleyana* Roezl.

The oil, obtained by T. C. Frye, of Washington, from the fresh needles and twigs of small trees and from the undergrowth to the extent of 0,8 to 1 %, is yellowish-green and has an odour reminding of limonene. It was investigated by J. W. Brandel in collaboration with M. Sweet[1]) and its constants were determined as follows: $d_{23°}$ 0,8680, α_D — 62,5°, acid no. 0, sapon. no. 86,6 corresponding to 30,3 % of bornyl acetate, sapon. no. after acetylation 92,1, from which a content of 32,2 % bornyl acetate, equivalent to 25,3 % of free borneol was erroneously calculated. In reality the bornyl acetate content was 34,6 % or 27,18 % of free borneol. No aldehydes could be traced by means of bisulphite. Fractionation of the oil showed it to consist chiefly of terpenes. The lower fractions, which had a pinene-like odour, yielded no nitroso-chloride. The fraction which boiled between 175 and 176° had a limonene-like odour, but (no doubt owing to the small quantity available), no tetrabromide could be obtained from it. The fractions boiling between 161 and 169° formed the chief part of the oil and contained camphene, m. p. 47°. The residue of distillation (b. p. above 190°) was saponified, whereupon the principal part boiled between 180 and 205°. As shown by the oxidation into camphor, (m. p. 171°; oxime m. p. 113°) it contained borneol. The higher boiling parts were of a deep-green colour.

Elemi Oil. Properly speaking, the name Elemi appertains only to the balsam from *Canarium luzonicum*, which is produced exclusively in the Philippines, and from which it is possible to obtain from 25 to 30 % of essential oil. But occasionally the name is also applied to similar balsams of other derivation, the name of the country of origin being added in that case. Thus, the Imperial Institute has recently had an opportunity of investigating so called "African Elemi", and the following particulars are published as to the result of the examination.

[1]) Pharm. Review **26** (1908), 326.

Elemi from Southern Nigeria, of which the botanical origin is unknown, varied in colour from white to pale yellow and yellowish green; it was of fairly solid consistency, and mixed with brown spots and vegetable residue.

A sample gave 0,6 % of ash, acid no. 55,3, sap. no. 71,9, the essential oil yield amounted to 8,1 %. This oil was of a straw yellow colour and contained ample proportions of phellandrene. The following constants are recorded: $d_{15°}$ 0,8686, specific rotation in a 100 mm. tube + 50° 30′. A second sample gave 0,53 % ash, acid no. 37,8, sap. no. 46,2; it contained 4,4 % of essential oil.

Uganda elemi, from *Canarium Schweinfurthii* was white to pale yellow and contained a considerable admixture of dark spots and wood, giving it a dirty appearance. The resin contained 0,3 % ash; acid no. 29,4, sap. no. 44,8 (both of these determined from a clean, picked sample). Steam distillation of this sample yielded 11,2 % of a pale, straw-coloured oil ($d_{15°}$ 0,8451; $\alpha_D([\alpha]_D?) + 79° 20'$) containing a large proportion of phellandrene.

According to these data, African elemi generally resembles Manila elemi, but it yields a much smaller proportion of volatile oil than does the latter. Possibly, if African elemi were carefully gathered and treated, it might compete with Manila elemi, but as the demand is only small it might be difficult to find an outlet for large quantities, should they be brought to market.

Essential Oils, Sicilian and Calabrian.

In accordance with our usual custom, we subjoin the report of our friend, Mr. Eduardo Jacob of Messina, to which reference has already been made in the preface.

Anyone who to-day on board of a rapid vessel passes through the Straits of Messina, will behold, as formerly, on the one side the smiling green chain of the Pelorian hills, while upon the other there rises majestically the forest-crowned mass of the Aspromonte. As in former times, so to-day, both shores appear to be adorned with a gay wreath of towns and villages, which impress their charming imprint upon the Straits of Messina. But, alas! when on the one or the other side the vessel closely approaches the shore! Where once stood flourishing cities, rich villages, and the smiling country seats of the wealthy of this beautiful corner of the earth, we now only behold confused masses of ruins; jagged remains of broken walls point towards the skies; churches, theatres, palaces, dwelling houses, even the lowly huts of the peasants, have fallen into dust and ruin, and beneath them, throughout the district, from 100 000 to 200 000 human beings lie buried, while the unfortunate survivors have fled from their in-

hospitable native land, and only a few of them, clinging lovingly to the soil upon which they were born, have established miserable new dwellings for themselves in huts made of branches or boards.

In the early morn of 28th December 1908 a terrific earthquake, the centre of which happened to be exactly within the sphere of the Straits of Messina, destroyed this beautiful region. At the very first shock, all that had been built up by the inhabitants in the course of centuries of endeavour, was almost levelled to the ground in the short space of a few seconds, and more than half of the population was swept away by the terrible forces of Nature.

Messina and Reggio have been completely destroyed; in neither town a single house is left standing which affords safe shelter to its inhabitants. Both cities were the offspring of ancient Greek culture; in former ages both were the emporia of the World's commerce of those days; and although in the course of the centuries they had gradually lost their international commercial pre-eminence, yet a flourishing traffic had been maintained in both places, especially in Messina, up to the present day. Among its other branches of trade, Messina — as is well known — held the chief place in the export of Sicilian and Calabrian essential oils. From 40 to 50 commercial firms, all possessing more or less capital, had gradually devoted themselves to this branch of business. Messina and Reggio supplied the whole world with the produce of the essential oil factories of Sicily and Calabria. It is therefore only natural that the earthquake of 28th December 1908 and the total destruction of Messina and Reggio, as well as of all the villages encircling the Straits which that calamity carried in its train, will bring about wide-spread changes in the commercial conditions of these essential oils.

Of the 40 or 50 commercial firms which devoted themselves to the essential oil trade, scarcely one-half is in existence at the present time, and these firms, if able to carry on business at all, will not be in a position to remain located in Messina, as the entire city is uninhabitable, and as, moreover, owing to the cessation of the general movement of trade in the port, opportunities for shipping goods to all parts of the world will in future be rare. It follows that within the next few years the essential oil trade will first of all transplant itself to the neighbouring towns of Catania and Palermo. But if the rebuilding of Messina, contrary to expectation, should be accomplished more quickly than is believed to be probable at the present time, there can be no doubt that the leading forces of the essential oil trade will again concentrate in this city, favoured as it is by its geographical situation and its excellent harbour.

With regard to the market position before and since the earthquake, the following is to be stated.

Although this year it is impossible at the present time to give accurate statistical figures, it may be maintained with justice and on good grounds that the export of essential oil in the course of the year 1908 has not only not fallen below that of the previous year, but has even slightly exceeded it. When the time of the new crop was approaching, the stocks of orange and bergamot oils were entirely exhausted, and only small parcels of oil of lemon were still in existence, these being in the hands of a few firm holders. The prospects of the new crop were, generally speaking, very good, and low prices for all kinds of essences were expected for the year 1909. The manufacture of the new season's orange oil had commenced as usual, although with some slight delay, at the beginning of October, and the oil content of the fruit being satisfactory, it yielded a rich output. Consequently prices fell to about 12 marks, a figure which no longer left any profit to the manufacturers, and which caused a partial cessation of the oil production.

This season the manufacture of oils of lemon and bergamot could only be commenced with considerable delay, because the trees had suffered greatly from the drought during the summer, and it was necessary that the fruit should be left to attain a certain size and degree of maturity. Just as the first small consignments of new fruit had been brought to market, the earthquake came and destroyed, at a single blow, all the existing conditions.

As in all previous years, so in the course of the summer and autumn of 1908, a lively business for future delivery in all varieties of essential oils had been developed, and when the time for the production of the new oil had arrived, consumers abroad were waiting anxiously for the new supplies, as the stocks of old oil which remained in their hands had been extremely reduced.

The destruction of the two cities of Messina and Reggio; the absence during many weeks of all detailed news with regard to the fate of the commercial firms which had entered into contracts with other countries; and finally the arrival of the news that most of these firms were no longer in existence and that their proprietors, with the whole of their families, except a few survivors, had met with a violent death, caused a panic in all the consuming countries of the world. This panic was stimulated by the uncertainty as to the legal position in which traders abroad were placed, most foreign firms having purchased oil in Messina and Reggio for forward delivery, and by the complete ignorance prevailing as to the conditions of production in Sicily, as a result of which it was, for example, thought possible that the lemon crop of the whole island might have been destroyed. Consequently, the stocks of oil which still remained in existence abroad were forced up to incredibly high prices, which partly reacted upon our island.

Palermo, the only commercial town in the island which was able to conduct an export business in essential oils in the first three weeks following the disaster, was besieged with orders from all parts, and in order to keep pace with the extraordinary pressure it was compelled to buy up, at ever increasing prices, whatever oil could be found outside the district affected by the earthquake.

Such an unnatural condition of things of course could not continue very long. Lemons are cultivated almost over the entire island of Sicily, and throughout Calabria, whereas the district visited and damaged by the earthquake was comparatively very small. The manufacture of oil of lemon is carried on in almost all places and villages throughout the island where lemons grow. The principal collecting centre for this produce up to the present time was Messina, but the greater part of the oils have always been pressed outside the Messina district. A strong and continued advance in the prices of oil of lemon was therefore almost impossible of realisation, as it was to be expected that the high prices themselves would result in an increased production.

The conditions in respect of orange oil were somewhat more serious. The season for the manufacture of this oil was almost past, the bulk of the manufactured oil was warehoused in Messina and Reggio, and it was therefore to be expected that with the destruction of these cities, considerable quantities of this oil had been lost. Such has in fact been the case. A not unimportant part of the orange oil of the current season is lost, and the quantity of this oil which is still for disposal is perhaps smaller than has generally been the case in previous years at the corresponding time.

But the situation in oil of bergamot especially appeared to be extremely serious and hazardous. The manufacture of this oil had scarcely commenced — in some districts it had not yet been begun at all — when the catastrophe occurred, and the only district in the whole world in which oil of bergamot is produced was in the very centre of the earthquake district, with the exception of a small portion, that is to say the districts of Melito, Bova, and Palizzi, which however have also been severely visited.

Scarcely a house is left standing from Palmi to Melito along the Western coast of Calabria, and in the gorges and valleys of the mountains and the uplands where formerly stood the flourishing little towns of Bagnara, Villa San Giovanni, Acciarello, Catona, Santa Catterina, Sbarre, Pellaro, Lazzaro, and Salino.

The preparation of bergamot oil was carried on in all these places; where but a short time previously diligent workers had pursued their occupations, death and destruction now reigned instead. Almost half the population has perished or received injuries; part of the survivors, panic-stricken, have sought refuge on board of the men-of-war of

different Nations which rushed to the rescue, and have been carried off to Naples, Malta, Palermo, or Genoa, and the remainder were for a long time unable to shake themselves free from the lethargy in which the sudden stroke of nameless ill-fortune had plunged them.

Thus the manufacture of bergamot oil came to a sudden end, even before it had reached its full development.

The dreadful earthquake shocks caused large quantities of the fruit to fall to the ground; this has mostly been left to rot unused. At certain points on the coast line, especially at Pellaro and Lazzaro, the sea broke upon the shore in waves as high as houses, tearing away trees, fruit, men, and beasts. Hence, part of the fruit on the trees has been destroyed before oil could be pressed from it.

While thus, with the exception of a few places, mental torpor and lethargy prevailed all along the Calabrian coast, business men had flocked to the spot from all countries of Europe, but especially from France, intent upon securing their requirements of bergamot oil for the season. Braving considerable privations and dangers, these men penetrated even into the smallest villages, buying up almost at any price every drop of bergamot oil upon which they could lay hands.

This fact again stirred up the dulled spirits of the unhappy people of Southern Calabria, and rendered them accessible once more to human emotions. Where up to the present they had only beheld and mourned death and destruction, the possibility of making good at any rate a portion of their losses again presented itself. The high prices which were paid for the oil by the foreign visitors induced the manufacturers to dig up their pressing-apparatus from the ruins; the labourers to start work again at double or treble their old wages. It is true that owing to scarcity of hands the work could only proceed very slowly and on a small scale, but nevertheless oil was produced, and will continue to be produced until the fruit falls rotten from the trees, and so long as the oil content leaves a profit on the cost of manufacture.

It is of course impossible at the present time to obtain reliable data anywhere, yet I believe that I shall not be far from wrong if I estimate this season's output of bergamot oil at barely one half of the quantity produced under normal conditions.

From the particulars set forth above the following conclusions may perhaps be drawn: —

Bergamot Oil. If indications go for anything, this oil should attain a high price this year, but this, of course, is also contingent upon the greater or less intensity of the demand from abroad during the next few months. The conditions of price of the article during the later months of the year will depend upon whether the fears will

be realised which are already entertained by experienced gardeners as to the result of the forthcoming crop.

The bergamot is an exceedingly sensitive, capricious tree, and the earthquake has had for its sequel a series of exceptionally severe, bleak storms and hurricanes, with snow, hail, and cold, all of which have affected the bergamot trees adversely. The trees have lost all their leaves and, apart from the remnant of fruit which they still carry, are standing bare and stripped, without foliage and without protection for the developing buds. Leaves must form before the trees can flower in the spring; if the flowers should appear on leafless trees, the setting and development of the fruit will be in extreme jeopardy. Experience shows that in such conditions poor harvests, or even crop failures, are the rule.

Lemon Oil. It is certain that an abundant crop of lemons is waiting to be gathered; consequently, unless the market should be exposed to artificial manipulations, the prices this year should not be subjected to unduly great fluctuations. This, of course, does not exclude the possibility that the prices now current may temporarily advance somewhat.

Mandarin Oil. Although very little has been produced this season, prices have remained comparatively low, and even to-day they do not exceed 40 marks per kilo.

Orange Oil, bitter, which was worth 12 marks last December, has since that time advanced considerably; the crop will be smaller than that of the preceding year.

Orange Oil, sweet. As mentioned above, no heavy supplies of this article appear to exist. The manufacturing season must be regarded as closed, and nothing is more likely than that, with some demand, prices may advance by several marks.

In a report by the Messina Chamber of Commerce on the agrumen oils (comprising bergamot, lemon, orange, and mandarin oils) examined between October 1st 1906 and January 30th 1908, E. Berté and G. Romeo[1]) give detailed particulars of the tests applied. We need not here enter fully into a description of the various methods used, as we have already dealt with their main features in previous Reports. We will therefore limit ourselves on this occasion to quoting, from the observations of the authors, the limits of value of the various constants.

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[1]) Annali del Laboratorio chimico della Camera di commercio ed arti della provincia di Messina. Messina 1908. From a copy kindly sent to us.

Lemon oil. $d_{15°}$ 0,856 to 0,861.

The rotation varies according to the producing district and the degree of ripeness of the fruit; generally speaking it ranges from + 58 to + 66° (20° C.). The fruit known as *Bastardoni* yields an oil of which the rotation occasionally falls below + 56°.

Evaporation residue 2 to 3,5 %; in the case of oil pressed by mechanical means up to 5 %.

The citral content varies, according to the methods employed, from 4 to 7,5 %.

Beginning of boiling at 175°.

Bergamot oil. $d_{15°}$ 0,880 to 0,887; up to a certain degree the sp. gr. is in direct proportion to the ester content. α_D + 7 to + 25°; usually between + 10 and + 20°.

Acid content (calculated as acetic acid) 0,15 to 0,2 %; in the case of old oils up to 4 %.

Ester content 33 to 44 %.

Evaporation residue 5 to 6 %.

Solubility: Pure bergamot oil dissolves in half its volume of 90 p. c. alcohol, most samples are soluble in their own vol. of 80 per cent. alcohol, the last-named degree of solubility indicates an oil of good quality [1]).

Beginning of boiling at 180° (normal press.) equal to 72° (20 mm. press.).

In order to detect the presence of French or American oil of turpentine, Berté and Romeo recommend that the first two fractions of 5 cc. each of 30 cc. oil be distilled off under reduced pressure, and that they be then tested in order to ascertain whether the first fraction has a higher rotatory power than the second. Further, the mean rotation of the two fractions should bear a definite relation to that of the original oil. This relation should alter with the rotation of the oil, and a table is given (compare original report), setting forth particulars under this head.

The following bergamot oils are of inferior quality:

a) The oil obtained from unripe windfalls (*bergamottella*). This oil is known as *nero di bergamotto*. It has a rather unpleasant, pungent odour, a dark colour and a high specific gravity; $d_{15°}$ 0,890 to 0,896.

Ester content between 20 and 35 %.

b) Distilled oil. This is obtained from the dregs (*feccie di bergamotto*) by distillation with water vapour. It is colourless or yellowish; $d_{15°}$ about 0,865; ester content 3 to 6 %.

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[1]) Of the many oils of the highest quality which we have examined in our laboratories, the minority were soluble in 1 vol. of 80 % alcohol. Compare Report November **1908**, 60.

Mandarin oil. $d_{15°}$ 0,854 to 0,858. α_D + 67 to + 73°.
α_D of the first half of the distillate averages 3° more than α_D of the original oil.

Orange oil, bitter. $d_{15°}$ 0,852 to 0,856. $\alpha_{D\,20°}$ + 88 to + 96°.
α_D of the first half of the distillate at least 3° higher than α_D of the original oil.

Orange oil, sweet[1]). $d_{15°}$ 0,847 to 0,852 $\alpha_{D\,20°}$ + 96 to + 98°.
α_D of the first half of the distillate at least 1° 30′ higher than α_D of the original oil.

Beginning of boiling at 176 to 177° (normal press.); 79 to 81° (20 to 30 mm. press.).

Lemon Oil. When criticizing the Swiss Pharmacopœia[2]) we pointed out, *inter alia*, that the statements there as to the determination of boiling points were insufficient. In order to obtain correct results, it ought to have been laid down that the entire mercury column must be surrounded by the vapours of the liquid. Fleissig[3]), by a series of most careful researches, has now experimentally established what are the differences shown in the case of oil of lemon according to whether the mercury column has or has not been wholly exposed to the vapours. He found that a thermometer protruding from the flask registered up to 5,5° less than one wholly exposed to steam, and that the requirement of the Pharm. Helv. IV that not more than 30 % of the oil of lemon must pass over at 170°, is fulfilled only in the latter case. As a result, he arrives at our own conclusion, that either a shortened thermometer must be used or the necessary corrections must be carried out. Fleissig also points out that the barometric pressure should be taken into account. The difference in the boiling point of water at Basle and St. Moritz, for instance, amounts to 5,3 °.

Sophisticators have taken advantage of the enormous advance in the price of oil of lemon to throw upon the market oils which are adulterated to an almost incredible extent. E. J. Parry[4]) reports on a whole series of such oils of lemon, the chief adulterants of which were mineral oil, castor oil, turpentine oil and also the terpenes of oil of lemon. Upon evaporation the samples adulterated with mineral oil left a residue of 30 to 50 % (specific gravity 0,878) showing the characteristics of paraffin. Normal oil of lemon leaves a residue

[1]) For the properties of this, and of bitter orange oil, as determined in our laboratories, see Report October **1906**, 35.

[2]) Report April **1908**, 127.

[3]) Schweiz. Wochenschr. f. Chem. and Pharm. **1909**, No. 5. From a copy kindly sent to us.

[4]) Chemist and Druggist **74** (1909), 121.

of only 2,3 to 3,5 %, so that the enormous proportion of the residue in the oils under notice affords a clue to the degree of sophistication. The castor oil was identified directly by its constants and its insolubility in petroleum ether, and in the samples adulterated with turpentine oil the addition was revealed at once when the optical behaviour of the first 10 % of the distillate was examined. For, whereas in the case of normal oils the difference in the rotation of the original sample as compared with the first 10 % of its distillate should be at most 5°, the values in this case differed by about 30°. The addition of lemon oil terpenes reduced the specific gravity from 0,852 to 0,856, besides reducing the citral content.

Orange Oil. The examination of 17 samples of oil of sweet orange, some of which were adulterated, caused E. Dowzard[1]) to express himself on the subject of the limits of value applying to the constants of sweet and bitter oils respectively. In this paper Dowzard arrives at the same conclusions which have been formed by ourselves. Having published our results at the time[2]), a reference to our former statements will now suffice.

Eucalyptus Oil. Oil of the Globulus variety as well as the ordinary Australian oil containing phellandrene was offered plentifully, but we do not believe that satisfactory transactions have been concluded, as the demand has only been of a very restricted character. Large stocks appear to have accumulated at all the principal trading centres, for which reason we regard a fall in the prices within the near future as extremely probable. Oil from *Eucalyptus maculata* var. *citriodora* has been more frequently asked for than it used to be. This oil is particularly esteemed on account of its high citronellal content, and the arrival of several important consignments has made it possible to satisfy the demand.

In the tenth part of the work edited by J. H. Maiden under the title *A critical revision of the genus Eucalyptus*[3]), a book to which we have already made repeated reference[4]), the following eucalyptus varieties are discussed: —

Eucalyptus piperita Sm. [synonymum: *Metrosideros aromatica* Salisb.].

Eucalyptus Sieberiana F. v. M.

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[1]) Americ. Journ. of Pharm. **80** (1908), 474.

[2]) Report October **1906**, 35.

[3]) Sydney 1908.

[4]) Comp. Reports October **1903**, 37; October **1904**, 39; April **1905**, 37; October **1905**, 33; April **1906**, 35; October **1907**, 53; April **1908**, 54.

Eucalyptus Consideniana Maiden.

Eucalyptus haemastoma Sm. [synonyma: *E. micrantha* D. C., *E. signata* F. v. M.].

Eucalyptus siderophloia Benth. [synonyma: *E. fibrosa* F. v. M., *E. ornata* Sieb.].

Eucalyptus Boormani Deane et Maiden.

Eucalyptus leptophleba F. v. M. [synonymum: *E. drepanophylla* F. v. M.].

Eucalyptus Behriana F. v. M. [synonymum: *E. pruinosa* Behr, non Schauer].

Eucalyptus populifolia Hook. [Synonyma: *E. micrantha* A. Cunn., non D. C., *E. populnea* F. v. M., *E. largiflorens* F. v. M., var. *parviflora* Benth., *E. bicolor* A. Cunn., var. *parviflora* F. v. M., *E. polyanthemos* Schauer, var. *populifolia* F. v. M.]

Eucalyptus Bowmani F. v. M.

A eucalyptus oil forwarded to the Botanical Institute at Buitenzorg[1]) which had been distilled by Dr. Carthaus in the Tengger Mountains of Java, showed $d_{26°}$ 0,996 (?) and $\alpha_D + 4° 18'$. At 150° the oil began to boil, up to 200°, 77 % had passed over, and from 200 to 240°, 16 %. The oil is said to consist principally of cineol.

In connection with the above we may refer to two eucalyptus oils which had also been produced in the Tengger Hills and which were sent to us by Dr. Carthaus in 1907. The first of these (which Dr. Carthaus surmises to have been derived from *Eucalyptus crebra*), was brownish yellow. It contained only a small proportion of cineol, and, besides this, phellandrene and cuminaldehyde (aromadendral?); $d_{15°}$ 0,9036, $\alpha_D - 20° 56'$, cloudy solution with 5 to 6 vol. of 80 % alcohol.

The second oil was derived from a long-leaved species, said to be *E. piperita* (?) and had a golden-yellow colour; $d_{15°}$ 0,8974, $\alpha_D - 28° 26'$. This oil gave a cloudy solution with about 8 vol. 80 per cent. alcohol; the solution in 90 per cent. alcohol, which is clear at first, opalesces when more than 1 vol. of the solvent is added. Cuminaldehyde (aromadendral?) and a great deal of phellandrene were found to be among the constituents; the sample was too small to allow of the determination of cineol. In the case of both oils the presence of phellandrene is evident already from the odour.

E. F. Harrison[2]) reports on a South African Globulus oil, produced by the Transvaal Eucalyptus Oil Co. of Johannesburg. This sample

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[1]) Jaarboek van het Departement van Landbouw in Nederlandsch-Indië **1907**, 66. Batavia 1908.

[2]) Pharmaceutical Journal **82** (1909), 4.

had a specific gravity of 0,9227 (15,5°) and an optical rotation of + 3° 17′. No phellandrene could be detected in it; on the other hand, it contained much cineol, the phosphoric acid process indicating a content of not less than 83,7 per cent. of this constituent.

Fennel Oil. The sluggish demand has induced the Galician fennel dealers to lower their previously exaggerated pretensions; hence, in the course of the closing months of last year, a very brisk trade ensued, so that it was possible to use considerable quantities for distilling purposes. The animated business transactions were impeded now and then by serious differences in the quality of the material, which, however, appear to have been mostly settled to the disadvantage of the suppliers. In view of the peculiarities of the people who occupy themselves with the exportation of fennel in Galicia, the minutest circumspection is needed in the agreements as to quality and delivery. Other supplies of fennel than the Galician did not affect our industry in the course of the past half year.

Geranium Oil. Considering the unsatisfactory state of the demand in the past year on the one hand, and on the other the fact that, in 1908, 46600 kilos of Algerian geranium oil were cleared by the customs as compared with 38700 kilos in 1907, it is not surprising that there has still been no improvement in the value. True, there was no lack of sensational rumours of unfavourable prospects due to bad weather-conditions and impending restriction of culture, but all these and similar tactics failed to draw the market from its state of indifference. Within the last few weeks the producers have been more accommodating than ever before and have tried to find buyers of large parcels for future delivery at the ridiculously low prices now ruling.

The commercial position of Réunion geranium oil is still more distressful. As is well known, this variety is less used in the manufacture of toilet-soaps than is the African kind, because owing to its characteristic odour as well as on account of its other properties it is not suitable for all purposes. We have already had occasion before now to point out that the World's annual consumption, which is estimated by the Syndicate at 30000 kilos, is actually far from reaching that figure, and we are able to confirm this assertion as the result of more recently received information. Seeing that notwithstanding this, the oil continues to be produced regardless of the demand, it is not surprising that within the last few years the prices have receded by one-half and that every hope of a return of the good old days is vanishing. The well-known "Syndicat de St. Pierre" continues to hold aloof from the market altogether, in the expectation of "better prices"; such, at any rate, is a statement of the *Bulletin commercial de l'Ile de la Réunion* of December 30th 1908.

It would be interesting to know what is the quantity still remaining in the hands of this Association, and upon what factors, with the present hopeless outlook for the article, the hopes of an improvement in prices are founded.

The following figures show the course of prices and the quantities exported during the last eight years: —

In 1901	exports	totalled	13953	kilos,	the	price	was	about	fr. 43
1902	„	„	17193	„	„	„	„	„	„ 36
1903	„	„	25323	„	„	„	„	„	„ 29
1904	„	„	27660	„	„	„	„	„	„ 27
1905	„	„	38334	„	„	„	„	„	„ 24
1906	„	„	31645	„	„	„	„	„	„ 22
1907	„	„	31247	„	„	„	„	„	„ 21
1908	„	„	34360	„	„	„	„	„	„ 20

In January of the present year a few transactions for future delivery were even put through at about 19 fr. The quality of the shipments during the past year does not call for comment.

In the course of the last few months the market in East Indian geranium oil has been fairly animated. The favourable reports of the forthcoming distillation, mentioned in our last Report, were revoked as far back as the month of November, and thenceforward the cif. quotations for palmarosa oil advanced from about 5/3 to about 7/-, but the latter figure appears to indicate high-water-mark for the present. It is said that in the producing districts severe fever-epidemics have decimated the ranks of the coolies engaged for cutting the grass, so that in many regions manufacturing has been interrupted. Ginger-grass oil of unimpeachable quality is hardly being offered at all, hence a great scarcity may occur shortly.

In one of our earlier Reports[1]) we have already called attention to the occurrence in American peppermint oils of dimethyl sulphide $(CH_3)_2S$, at the same time giving some details as to the reactions for the determination of this compound. Recently we have also succeeded in detecting the presence of this body in Réunion, as well as in African, oil of geranium.

On the occasion of working up a large parcel of Réunion oil we obtained from the first runnings a fraction with a b. p. of 30 to 60°, which possessed in a marked degree the unpleasant odour of dimethyl sulphide. By dint of repeated careful fractionation, pure dimethyl sulphide, b. p. 37°, was recovered from this fraction. It was identified

[1]) Report October **1896**, 58.

by the well-known reactions with chloride of mercury, and chloride of platinum. The presence of dimethyl sulphide in African oil was confirmed in a similar manner.

Mr. J. H. Burkill, of the Indian Museum, Calcutta, who had already on a former occasion[1]) been kind enough to send us oil distilled from *Cymbopogon Martini* Stapf. (*Andropogon Schoenanthus* Flück. & Hanb., non L.) has again had the courtesy to forward us nine similar oils, eight of which, upon closer examination, proved to be palmarosa oils, while the ninth was an oil of gingergrass. The oils specified in the subjoined table under nos. 1 to 5 are of special interest because they were personally collected at the stills by Burkill in several parts of the Central Provinces and hence must be regarded as unquestionably genuine samples.

Distillates of *Cymbopogon Martini* Stapf.

No.	Vernacular name	Origin, Province	$d_{15°}$	α_D	$n_{D\,20°}$	Acid no.	Ester no.	Total Geraniol	Solubility in 70 p.c. alcohol
1.	"Motia"	Deogaon	0,8895	$+0°16'$	1,47274	1,8	40,3	92,65	1,7 vol.
2.	„	Behali	0,8891	$+0°15'$	1,47313	1,5	34,7	94,65	1,6 „
3.	„	Lebada	0,8895	$+0°17'$	1,47254	1,6	38,4	93,4	1,7 „
4.	„	Arnadi	0,8889	$+0°55'$	1,47264	1,0	39,4	93,9	1,8 „
5.	„	Balkhara	0,8924	$+1°18'$	1,47313	0,9	38,9	92,0	1,7 „
6.	„	Ellichpore	0,8896	$+0°12'$	1,47392	1,1	12,4	90,9	1,7 „
7.	„	„	0,8911	$+0°12'$	1,47313	0,8	40,0	93,9	1,7 „
8.	„	„	0,8917	$-0°53'$	1,47470	0,8	17,3	87,9	1,6 „
9.	"Sofia"	„	0,9024	$+3°54'$	1,47163	2,3	15,0	89,5	1,7 „

According to this table, all the "Motia" oils proved to be good palmarosa oils of normal characteristics. Their geraniol content is very high; in fact, it only falls below 90% in sample no. 8. The oils differ to some slight degree from each other as regards odour, but they nevertheless all possess a pure palmarosa character, and in this respect also they answer all requirements, except sample no. 6, which has a slightly musty odour. Sample no. 9, "Sofia" is a gingergrass oil of exquisite quality, and therefore its composition differs entirely from that of the "Motia" oils. As we have already on previous occasions[2]) reported in detail on this point, as well as on the botanical origin of the "Motia" and "Sofia oils", a reference to these Reports will now suffice.

Gurjun balsam Oil. A balsam sent to us under the designation of Cochin Wood Oil was absolutely identical with ordinary gurjun balsam, both as regards colour and odour, and as regards its constants. The

[1]) Report April **1907**, 58.
[2]) Reports April **1904**, 56; October **1904**, 52; April **1905**, 55; April **1907**, 30.

balsam, which was of a brown colour, with a greenish fluorescence, showed the following characteristics: $d_{15°}$ 0,9633, α_D — 37° 30′, $n_{D20°}$ 1,51236, acid no. 7,8, ester no. 2,9. Even with absolute alcohol it only gives a cloudy solution, from which flocculent separation takes place quickly. When the sample was distilled by steam it yielded 69,9 % of a lemon-yellow oil, possessing the following properties: $d_{15°}$ 0,9248, α_D — 61° 48′, $n_{D20°}$ 1,50252, acid no. 0, ester no. 1,6; soluble in 9 vols. and more of 95 per cent. alcohol. At normal pressure (741 mm.) 86 % passed over between 260 and 265°, and 6 % between 265 and 269°.

Oil from Helichrysum angustifolium Sweet. From Hungary we received a sample of oil which showed almost similar characteristics as did an oil from the same plant distilled by ourselves and described by us at the time[1]). It possessed the following constants: $d_{15°}$ 0,9084, α_D + 4° 25′, $n_{D20°}$ 1,47450, ester no. 134,0, soluble in 6 to 7 vols. and more of 85 per cent. alcohol. The slight differences between this oil and that previously examined are possibly due to differences in the state of maturity of the plant or in the method of distillation.

Oil of Illicium religiosum. Some time ago we had an opportunity of investigating Japanese star anise oil[2]) distilled from the fruit of *Illicium religiosum* Sieb., a drug which was formerly often used as an adulterant of genuine star anise. The oil differs from oil of Chinese star anise chiefly in the fact that, unlike the latter, it contains scarcely any anethol, while its principal constituent is safrol of which Chinese oil contains only traces. The Japanese oil, therefore, congeals in the freezing mixture only at about — 18°, with separation of safrol. When subjected to fractional distillation under 3,5 mm. pressure, also a fraction containing cineol was obtained. With concentrated resorcinol solution this fraction gave the characteristic cineol-resorcinol combination. Another fraction appeared to contain linalool, but owing to the smallness of the sample available the presence of this could not be ascertained with certainty. The constants of the oil were as follows: $d_{15°}$ 0,9848, α_D — 0° 50′, acid no. 1,8, ester no. 12,9, soluble in 5 to 6 vols. and more of 80 per cent. alcohol, paraffin being separated.

Behaviour on fractionating (3,5 mm. pressure): —

1.	to 40°	21,6 %	α_D + 6° 20′	Cineol fraction.
2.	40 to 65°	8,0 %	α_D + 1° 14′	Contains linalool (?).
3.	65 to 79°	17,2 %	α_D — 5°	
4.	79 to 83°	32,0 %	α_D — 4° 6′	Safrol fractions.
5.	83 to 90°	4,6 %	α_D — 3° 30′	
6.	Residue	16,6 %		

[1]) Report October **1903**, 76.
[2]) Report October **1902**, 80.

Juniper Oil, empyreumatic (Cade Oil). In our last Report[1]) we referred at length to a paper by Pépin on the origin, preparation and examination of cade oil. A publication of this kind deserves the warmer welcome because it tends to revive the interest in this oil. If less has been heard in recent years of the excellent action of this oil in skin-diseases, which has been praised by leading dermatologists, the reason is simply that the adulteration of cade oil has lately assumed incredible dimensions and that a really pure article is nowadays almost the exception. In most cases, therefore, it may be taken for granted that the non-success of cade oil which has been observed in dermatological practice is due to its admixtures. Probably even it often happens that other empyreumatic distillates are used in lieu of cade oil, and with the present insufficient knowledge of the properties and composition of the article it is difficult to recognise such substitutes invariably and with certainty. This matter was all the more perplexing because up to now it has been almost impossible to obtain a really authentic material which would serve as a standard in judging cade oil. It is therefore undoubtedly to Pépin's credit that he should try to re-establish the reputation of genuine cade oil by showing, from material distilled by himself, what should be the requirements of a genuine oil.

We have followed the whole question with great interest and have at once taken the necessary steps to procure a guaranteed pure cade oil, which we have recently begun to list. We also refer to this oil here in order that, by bringing it to the notice of the widest possible circle, we may induce dermatologists to experiment again with pure cade oil with renewed confidence.

The examination of a sample of the oil gave the following results: $d_{15°}$ 1,0309, acid content (calculated for acetic acid) 0,64 %, permanently clearly soluble in any proportion of chloroform and anilin. In the case of solutions in ether, benzene and glacial acetic acid, which at first are also clear in any proportion, precipitates occur after some lapse of time. An equal volume of oil and of 90 or 95 per cent. alcohol is required for solution, and here the solution remains clear when further quantities of the solvent are added, but in both cases a flocculent separation occurs after some time. In boiling, the oil behaved as follows: —

760 mm.		3 mm.	
150 to 300°	about 55 %	80 to 150°	about 53 %
300 „ 350°	„ 12 %	150 „ 175°	„ 12 %
Residue	„ 31 %	Residue	„ 32 %

[1]) Report November 1908, 24.

The discrepancies existing between our own and Pépin's observations are explainable by the fact that so far only few oils have been examined, and that certain fluctuations of course also occur in pure oils. A considerable quantity of experimental material and further research into the whole question will be necessary before it becomes possible to establish really authoritative constants for cade oil. The marked difference between Pépin's record of the behaviour on boiling and our own is due to the different manner in which the thermometer was handled. While in the case of our investigations the whole of the mercury column was exposed to the vapours, Pépin placed his thermometer so that 230° was above the stopper. When operating in this manner, we found the fraction passing over between 150 and 300° to be 60%.

Kobushi Oil. A kobushi oil examined by Y. Asahina and H. Nakamura[1]), which had been distilled in the Japanese province of Shizuoka from one year old twigs, showed in some respects considerable differences from the kobushi oils which had been examined so far[2]). This oil was bright yellow and had an odour reminding of citral. $d_{15°}$ 0,892; α_D + 6° 8′; acid no. 4,3; sap. no. 19,1; sap. no. after acetylation 56,48, soluble in 1,4 vol. of 85 per cent. alcohol, further addition of the solvent produced opalescence. It was found to possess the following constituents: citral (6 to 7%, α-citryl-β-naphthocinchonic acid, m. p. 197 to 200°), eugenol (benzoyl compound, m. p. 69°), cineol (cineol iodide, m. p. 112 to 113°, cineolic acid, m. p. 195°) and, as principal constituent, methylchavicol which yielded homoanisic acid (m. p. 84 to 85°) and anisic acid (m. p. 184°) when oxidised with permanganate of potash. According to the authors, the oil may also contain pinene, because the fraction boiling between 150 and 160° yielded traces of a nitroso-chloride which could not be more closely characterised on account of its scarcity. The authors found the following acids: caprinic acid (silver salt, readily soluble in hot water, 38,52% Ag) and oleic acid (silver salt, insoluble in hot water, soluble in hot alcohol, 27,54% Ag). It is worthy of note that the oil examined by Asahina and Nakamura contained no anethol, a substance of which the presence in kobushi oil has been proved quite clearly by ourselves as well as by Charabot and Laloue. We identified the anethol direct by its m. p. 22 to 23°. Asahina and Nakamura employed for purposes of identification picric acid among other substances, whereas according to Bruni and Tornani[3])

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[1]) According to the Journ. of the Pharm. Soc. of Japan, No. 322, Dec. **1908**. Tokyo.

[2]) Report October **1903**, 78; April **1908**, 61.

[3]) Compare the abstract in Chem. Zentralbl. **1904**, II. 954.

this reacts only with bodies having propenyl side-chains, but not with bodies having allyl side-chains. Whereas anethol combines with picric acid in orange-red needles, melting at 68 to 70°, the experiment in the case of all fractions of the oil in question remained without any result whatever.

The absence of anethol, however, is not the only respect in which this oil differs from the samples previously examined. It is also lighter and, opposite to the others, dextrorotatory. Furthermore, the occurrence of eugenol and of the acids referred to above are new features in kobushi oil. It is possible that these variations may be partly accounted for by the conditions under which the distilling material was grown, or by the fact that in the distillation of the oils previously examined a larger proportion of leaves was used than in the case of the sample referred to above.

The statement may also be of interest that the flower-buds and the stalks of *Magnolia Kobus* are an old-fashioned Japanese remedy, which was formerly used against headache, under the name of *Shin-i*.

Oil of Laurel leaves. In addition to the oils distilled in France and Germany, the produce of other countries is now also frequently seen on the market, oils of quite suitable quality being offered from the Mediterranean Islands and from Palestine in particular. The following table gives a graphic view of the characteristics of the various oils:

	$d_{15°}$	α_D	$n_{D\,20°}$	Acid no.	Ester no.	Ester no. after acet.	Solubility
German and French	0,915 to 0,932	— 15° to — 18°	1,469 to 1,477	up to 2,0	28 to 43	58,3 to 77,7	in 1,3 vol. 80 p. c. alc., some (esp. French) samples in 3 to 10 vol. 70 p. c. alc.
Fiume . . .	0,9281	— 13° 52′	1,47156	1,0	31,9		in 2,5 vol. 70 p. c. alc. and more
Corfu	0,9177 to 0,9211	— 16° 40′ to — 21° 40′	1,46862 to 1,47107	up to 1,5	29,8 to 43,8	36,2 to 82,5	in 1 volume 80 p. c. alc., mostly in 3 to 6 vol. 70 p. c. alc.
Cyprus . . .	0,9405	— 5° 40′	1,47372	1,6	25,3	95,6	in 2 to 3 vol. 70 p. c. alc. and more
Palestine . .	0,916 to 0,924	— 14° to — 21°	1,46516 to 1,46575	up to 2,2	21 to 49	43,2 to 81,4	in 1 to 2 vol. 80 p. c. alc., some in 4 to 7 vol. 70 p. c. alc.
Asia Minor .	0,9268	— 15° 50′	1,46575	0,8	34,8	60,1	in 1 volume 80 p. c. alc. and more

Lavender Oil. Business in lavender oil had dragged on quite lifelessly during the past five months. As a result of the bad state of trade, buyers showed themselves extremely reticent, but on the

other hand many producers also refused to sell at the low prices which ruled as a consequence of the abundant crop, and kept back their holdings in the hope of a more profitable opportunity of disposing of them. These expectations, however, have not been realised, for, leaving out of account a slight improvement of the market which made itself felt in the beginning of February, when several firms in Grasse were compelled to cover themselves, and which has again been perceptible lately, the article is, generally speaking, thoroughly neglected. In the principal producing districts the winter was exceptionally severe, and the snowfall the heaviest on record for forty years. In some parts of these districts, people were cut off from the outer world for a long time and several parcels of lavender oil which we had on the way suffered considerable delay in transport. As a result of timely and important purchases, we have been enabled to reduce our quotations to some slight extent.

We have previously referred to the observations of Birckenstock[1]) on the effects exerted by the hybridising of *Lavandula vera* D. C. and *L. Spica* D. C. upon the properties and the constitution of the essential oil.

The paper of H. L. Visser on the examination of lavender oils, to which reference was made in our last Report[2]), has called forth some comments by W. J. de Maar[3]). The latter agrees with Visser that the Dutch Pharmacopœia has fixed too low a maximum limit (0,890) for the specific gravity of the oil, but he does not believe that by demanding a minimum content of 35% of linalyl acetate the Pharmacopœia will exclude the most of the lavender oils of commerce, because he himself has had no difficulty in obtaining oils which fulfil this condition, provided he paid corresponding prices. De Maar expresses his astonishment that Visser's experiences in regard to this matter should have been so unsatisfactory, and that, in spite of the abnormal properties of the commercial oils examined, Visser should have had no doubts as to their purity.

We should not again have referred to Visser's paper, were it not that that investigator had in the meantime published in the *Pharm. Weekblad* a contribution[4]) in which, among other things, he seeks to controvert our criticism. Visser maintains here that we have misinterpreted the object of his article, as the publication of his researches was merely intended to show that lavender oils occur in the wholesale

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[1]) Report October **1906**, 43.
[2]) Report November **1908**, 80.
[3]) Pharm. Weekblad **45** (1908), 1536. From a copy kindly sent to us.
[4]) Pharm. Weekblad **46** (1909), 39.

trade which do not satisfy the requirements of the Dutch Pharmacopœia. No objection whatever could have been raised against a publication having such a purpose, if Visser had not made the mistake of regarding adulterated oils as pure, and of drawing conclusions from these erroneous premisses. In order to avoid confusion, it was obviously necessary to correct such a mistake, although it can be understood that the reason why Visser believed the oils to be pure was that they were alleged to come from reliable sources. One of the oils in question was even reputed to have been obtained from us as "Ol. lavand. Ph. Ned. IV", but its characteristics were such ($d_{15°}$ 0,900, α_D — 13,5°, ester content 38,9 %) that we feel bound here to give an explicit denial to this assertion. We declare that lavender oils of such a description would not be supplied, and have never been supplied, by us. Unfortunately the firm to whom we are said to have supplied the oil had nothing left of it, so that we are unable to clear up the misunderstanding involved in the assertion.

With the object of increasing the interest in lavender growing in the South of France, L. Lamothe has published a new article entitled "*la Lavande*" [1]) which, broadly, contains all the information which we have already quoted from this author's publications on previous occasions [2]). A new statement is that in the principal lavender growing districts a syndicate of distillers has been formed for the purpose of undertaking the cultivation and distillation of lavender on rational lines. Since last year this syndicate has already acquired a number of modern stills, and it is said to have produced oils with an ester-content of from 40 to 57 %. Its sphere of activity extends over the entire region of the Upper Drôme, the Hautes-Alpes and the Basses-Alpes, which is known to produce by far the best oils. Adjoining this district is that of the Italian Alps, with a lavender oil of inferior quality, and, as a third zone of cultivation, the region of the Lower Drôme and the Vaucluse.

The output of oil in the various Cantons is somewhat as follows: La Motte-Chalançon and Séderon, 4500 kilos each; Luc-en-Diois 3000 kilos; Bourdeaux, Saillans, and Rémuzat each 2500 kilos; Dieulefit, Nyons and Buis-les-Baronnies each 2000 kilos oil of the best lavender; the Cantons of Pierrelatte, Grignan, and St. Paul-Trois-Châteaux together 2500 kilos of lavandin oil [3]). As already stated in our last Report [4]), the total output of the Department of the Drôme is therefore on the average 28000 kilos of oil.

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[1]) La Parfumerie Moderne **1** (1908), 3.
[2]) Report November **1908**, 76.
[3]) Report October **1906**, 44.
[4]) Report November **1908**, 78.

The principal centres of production in the department of the Basses-Alpes, with a total yield of about 12000 kilos of oil of exquisite quality, are the Lure Mountain chain, together with Cruis, Mallefoûgasse, St.-Etienne, Banon, Forcalquier, Châteauneuf, Valbelle, Sisteron, the district of Barrême, Clumac, Lambruisse, Tortonne, Castellane, and Senez.

Lemongrass Oil. Since we last reported on this article, the quotations have moved round about 2 d. per oz., with slight upward and downward fluctuations. An attempt to engineer a demand for lemongrass oil on the occasion of the Sicilian disaster, on the ground that this oil forms the raw material for citral, must be pronounced a complete failure. Considerable stocks of lemongrass oil are held in Europe, and as, in spite of the low values, the growers in India continue cheerfully to produce in spite of the low value, there seems for the present to be no prospect of more remunerative prices.

In our previous Report (p. 82) we stated that, according to de Jong's researches, Java lemongrass oil, although giving a clear solution with 2 parts of 70 per cent. alcohol immediately after distillation, becomes less soluble already after a few days; and that de Jong is of opinion that this change is due to the polymerisation of a terpene. F. Watts and H. A. Tempany[1]) have experienced similar results with oils distilled in the West Indies. They also attribute this phenomenon to the polymerisation of a hydrocarbon which, they think, is perhaps identical with myrcene.

As we have repeatedly stated in our Reports, the same difficulty of solubility is manifested by the lemongrass oils distilled in Brazil, Mexico, Africa etc., all of which are currently termed "West Indian" lemongrass oils. This want of solubility finally becomes so pronounced that even solutions of the oil in absolute alcohol, which are clear at first, become cloudy when more of the solvent is added. On the other hand, the so-called Malabar, Cochin, or Travancore lemongrass oils (= "East Indian" lemongrass oil) remain readily and clearly soluble in 70 per cent. alcohol even a long time after distillation. Stapf[2]) has ascertained that the difference in the behaviour of the oils is due to the fact that the plants of origin are not the same, the Malabar oil being obtained from *Cymbopogon flexuosus* Stapf, and the West Indian oil from *C. citratus* Stapf. According to Watts and Tempany[3]), the Botanic Stations on the Leeward islands are engaged in the experimental cultivation of *Cymbopogon flexuosus* (Cochin grass) in order to

[1]) West Indian Bulletin **9** (1908), 265. From a copy kindly sent to us.
[2]) Comp. Report April **1907**, 58.
[3]) West Indian Bull. **9** (1908), 267.

make it possible to obtain a lemongrass oil which should be equal in every respect to the Malabar oil. The grass grows well there, and the fact that four samples of oil from Cochin grass grown in Antigua and Montserrat did not as yet reach the high citral content desired (they contained respectively 53, 63, 64 and 68 %) is ascribed by Watts and Tempany to the insufficient degree of ripeness of the grass, experiments with "West Indian" grass having shown that not only the oil yield but also the citral content of the oil increase in proportion to the ripeness of the grass. 72,5 kilos of a grass grown in Antigua, three months old, yielded upon distillation 139 cc. of oil with 58 % of citral, while an equal weight of one year old grass yielded 206 cc. of oil with 69 % of citral. The most favourable conditions for harvesting Cochin grass are to be determined still. From the results hitherto obtained by the experiment station it appears that from two to three crops may be gathered in the course of the year, each cutting producing from 6000 to 8000 lbs. of grass per acre. The oil yield was found to be from 0,2 to 0,26 %.

Two illustrations of the distilling process given in the *Bulletin* are evidently intended to represent a general indication of the mode of distilling volatile oils, the various parts shown (still, rising tube, condenser, and receiver) not being given to scale.

As mentioned in our last Report[1]), experiments similar to those of Watts and Tempany have been made in Barbados with most favourable results. A lemongrass grown by the Government laboratory in that island from Cochin seed yielded a readily soluble oil and very rich in citral.

To a previous note[2]) on an oil said to be derived from *Andropogon Schoenanthus* which was examined in the Government laboratory at Antigua and behaved altogether abnormally, being in no way ascribable as Palmarosa oil, but rather resembled lemongrass oil, we are now able to add the statement that the oil in question was the product of a lemongrass four years old, which had never previously been cut. We take this statement from a comparative table dealing with a series of West Indian lemongrass oils, which has been prepared by Watts and Tempany.

We quote from a paper read in Berlin by Prof. Preuss[3]) the statement that the experimental cultivation of *Andropogon citratus* (author?) in New Guinea has shown profitable results, and that the distillation of lemongrass oil is now to be commenced there on an

[1]) Report November **1908**, 82.
[2]) Report October **1902**, 50.
[3]) Berichte d. deutsch. pharm. Ges. **19** (1909), 25.

extensive scale. In the course of the last few years we have frequently had occasion to examine similar lemongrass oils from the German Colonies in the Pacific and have found them to equal, as regards their properties, the oils which we have received from the West Indies, Mexico, Brazil, Java, Africa, etc. As their aldehyde content is fairly high, the New Guinea oils will be very suitable for the preparation of citral. Four samples of New Guinea oils showed the following constants: —

	I	II	III	IV
$d_{15°}$	0,8850	0,8852	0,8923	0,8810
α_D	— 0° 15′	— 0° 22′	— 1° 15′	— 0° 11′
Citral content:	78 %	78 %	65 %	76 %

Solubility: All the oils are insoluble in 70 per cent. alcohol; with 80 and 90 per cent. and even with absolute alcohol they give at first clear solutions, but when more of the solvent is added cloudiness or opalescence sets in.

Another lemongrass oil which was sent to us for report from Uganda (British East Africa) possessed exactly similar properties: $d_{15°}$ 0,8703, $\alpha_D \pm 0°$, citral content 67 per cent., insoluble in 70 and 80 per cent. alcohol; with 90 per cent. and with absolute alcohol it dissolved clear at first, becoming turbid when more solvent was added.

Limette Oil. We learn from the *Pharmaceutical Journal*[1]) that in the island of Dominica the lime industry has reached an extraordinary development. In 1907 the crop of fruit reached 272 229 barrels, an increase of 32 000 barrels as compared with 1906. The area under cultivation has been greatly extended, and it is estimated that in the year just closed from 400 to 450 acres were under cultivation. Lime-growing is also steadily increasing in the island of Montserrat, where it has again reached its former importance. The fruit is chiefly grown for its juice, limette oil being a by-product.

Linaloe oil. The price-conditions of this article persistently decline to assume a more favourable aspect. It is true that the importers have occasionally cleared out small parcels at less than the market-rate, and that more favourable purchases could at times be made, especially in Paris, but when, owing to the catastrophe in Southern Italy, an extraordinary demand set in for linalyl acetate as a substitute for bergamot oil, the quotations rushed up to the extent of 20 %. But now that the effects of the earthquake have been to some extent overcome, and bergamot oil is again available, it is probable that there will be no further call upon the linaloe oil market for this particular purpose. Hence the position is likely to become quieter again before long.

[1]) Pharmaceutical Journal **82** (1909), 19.

It will be remembered that a few years ago[1]) we reported repeatedly on dextrorotatory linaloe oils which, as regard their other characteristics, behaved like normal oils. The constants then observed lay within the following limits: $d_{15°}$ 0,8783 to 0,8816, α_D + 2° 54′ to + 8°, $n_{D\,20°}$ 1,46149 to 1,46209, acid no. 1,2 to 1,7, ester no. 3,74 to 20,0, soluble in 1,6 to 2,0 vols. and more of 70 per cent. alcohol. Similar oils were afterwards observed by Parry and Bennett[2]) and by Simmons[3]). Closer examination of one specimen has shown to us that as regards their chemical composition these oils differ from the lævorotatory oils which had been found in commerce up to that time, only by their content of d-linalool and l-terpineol (m. p. 35°); for the rest, like the others, they contained geraniol and nerol. From a communication which has appeared in the *Berichte* of Roure-Bertrand Fils[4]) it now appears though as if the question of the origin of these dextrorotatory linaloe oils has been solved, inasmuch as the examination of an authentic oil distilled from the seed of the linaloe tree produced a result identical with that of our examinations referred to above. This oil from seed contained besides l-linalool, l-terpineol, nerol and geraniol, and possessed the following constants: $d_{15°}$ 0,8858, $\alpha_{D\,26°}$ + 1° 30′, $n_{D18°}$ 1,4655, soluble in 1,5 vol. and more of 70 per cent. alcohol, acid. no. 3,4, sap. no. 34,3 (corresponding to 10,8 % $C_{10}H_{17}OCOCH_3$). From these results the authors consider themselves warranted in assuming that the seed of the linaloe-tree yields a dextrorotatory oil, and that the oils referred to above must therefore be regarded as linaloe seed oils. The future will show whether this assumption is correct. We will only, on this occasion, observe in parentheses that in the year 1899 we received from Venezuela an oil said to be prepared from linaloe-seed which possessed the following constants: $d_{15°}$ 0,893, α_D — 2° 26′, sap. no. 86,2, soluble in 2,5 vols. of 70 per cent. alcohol, producing a slight opalescence with more than 5 vols. We are, however, not in a position to make an authentic statement as to the origin of this oil.

When working-up a considerable parcel of linaloe oil, we obtained, after saponification of the oil with alcoholic potash and subsequent distillation by water vapour, an alcoholic first running, from which after addition of water, we were able to separate an exceptionally light, faintly optically active oil ($d_{15°}$ 0,7727; α_D + 1° 46′). It commenced to boil at 42° in a moderate vacuum (18 mm. press.) and

[1]) Report October **1904**, 56; October **1905**, 47.
[2]) Chemist and Druggist **68** (1906), 544; Report October **1906**, 47.
[3]) Chemist and Druggist **68** (1906), 584; Report October **1906**, 47.
[4]) Berichte of Roure-Bertrand Fils, October **1908**, 18.

distilled at ordinary pressure between 108° and 170°. Its constants, as well as its behaviour when boiled with sodium warranted the assumption that we had here to deal with unsaturated aliphatic hydrocarbons, and the behaviour towards bromine pointed to the same conclusion. By repeated fractionation over sodium under normal pressure we obtained optically inactive fractions of such abnormally low specific gravity that in the circumstances they could only be regarded as hydrocarbons of petroleum. The elementary analysis showed in fact that the portions boiling between 120 and 145° consisted of octylene and nonylene and their isomers. One fraction, possessing the b. p. of octylene and the following constants: $d_{15°}$ 0,7396, $\alpha_D \pm 0°$, $n_{D\,20°}$ 1,41255, b. p. 122 to 125°, yielded upon analysis the subjoined values: —

I. 0,1491 g. sbst.: 0,4645 g. CO_2, 0,1931 g. H_2O.
II. 0,1663 „ „ 0,5195 „ CO_2, 0,2165 „ „

	Found I.	Found II.	Calculated for C_8H_{16}
C	84,96 %	85,20 %	85,70 %
H	14,39 %	14,46 %	14,28 %

The physical constants and the analytic values of a fraction with the b. p. of nonylene likewise agreed completely with those of this olefine: $d_{15°}$ 0,7477, $\alpha_D \pm 0°$, $n_{D20°}$ 1,41808, b. p. 139 to 142°.

0,1648 g. sbst.: 0,5144 g. CO_2, 0,2169 g. H_2O.

	Found	Calculated for C_9H_{18}
C	85,13 %	85,70 %
H	14,62 %	14,28 %

We may leave it an open question whether octylene and nonylene are to be regarded as normal constituents of linaloe oil, or whether hydrocarbons of petroleum were present in these particular fractions; but in any case it is very improbable that such hydrocarbons had been added to the linaloe oil as adulterants, because for this purpose the quantity found present (1 to 2 per cent) would have been too small. Possibly the occurrence of these hydrocarbons in linaloe oil may have been due to the oil having been shipped in dirty tins which had previously contained petroleum. At the same time we may take this opportunity of pointing out that Burgess and Page[1]) had already found octylene to be present in oils of lemon and bergamot.

We were further able to determine that in the lowest boiling fractions of linaloe oil there occurs, besides the terpene proper, an olefinic terpene ($C_{10}H_{16}$) which is probably identical with myrcene.

[1]) Journ. chem. Soc. **85** (1904), 1327; Report April **1905**, 31 and 35.

A fraction which served for the purpose of detecting the presence of this body showed the following constants after having been freed from methylheptenone: $d_{15°}$ 0,8243, α_D + 0° 32′, $n_{D20°}$ 1,46476, b. p. 169 to 173° (atmospheric press.), b. p. 63 to 65° (16 mm. press.). Elementary analysis gave the following results: —

0,1744 g. sbst.: 0,5628 g. CO_2, 0,1872 g. H_2O.

	Found	Calculated for $C_{10}H_{16}$
C	88,01 %	88,23 %
H	11,92 %	11,77 %

The oil under discussion shares with the well-known olefinic terpenes the property of resinifying quickly when left exposed to the air, or when distilled under normal pressure. When re-distilled over sodium the hydrocarbon passed over between 172 to 183°. Under the conditions formulated by Enklaar[1]) for the preparation of myrcenol from myrcene, the terpene, when warmed for 3 to 4 hours to 40° with glacial acetic and sulphuric acids, yielded an acetic ester with a b. p. of 80 to 87° (4 mm. press.) from which, upon saponification, there resulted an alcohol possessing the properties of myrcenol[2]). We determined: b. p. 79 to 83° (3 to 4 mm. press.), $d_{15°}$ 0,9061, $n_{D20°}$ 1,47995. The alcohol possessed the markedly characteristic and pleasant odour (only distantly reminding of linalool), which also belonged to a preparation of myrcenol made by us for purposes of comparison. Unfortunately, in the case of both preparations we vainly endeavoured to bring to crystallisation the oily phenyl urethanes which had been obtained. A negative result also attended repeated efforts to identify the dihydro-myrcene (which had been obtained from the terpene by reducing it with sodium and alcohol) by the tetrabromo dihydro-myrcene (m. p. 88°) prepared according to Enklaar's directions. The product of reduction possessed the following constants: b. p. 169 to 173°, $d_{15°}$ 0,7849, $n_{D20°}$ 1,44378, which agree fairly well with those given by Enklaar for dihydro-myrcene.

The terpene which was found in association with the olefinic terpene, and to which reference has been made above, could neither be characterised by a bromine derivative nor by a nitroso-chloride or a nitrite, but the optical rotation α_D + 8° 41′ of a fraction boiling between 65 and 72° (16 mm. press.) indicated its presence.

Linaloe Oil, Cayenne. The only fact known up to the present with regard to the chemical composition of Cayenne linaloe oil was that its chief ingredient consisted of linalool. In a paper by Theulier[3])

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[1]) Compare Enklaar: *Over Ocimeen en Myrceen.* Dissert. Utrecht 1905; Report April **1906**, 109.

[2]) Ibidem.

[3]) Rev. gén. de Chim. III. **6** (1900), 262; Report April **1901**, 40.

which appeared some years ago, Cayenne linaloe oil was stated to differ from the Mexican variety by the absence of methyl heptenone, terpineol and geraniol. Having had occasion to examine Cayenne linaloe oil ourselves, we have ascertained that Theulier's observation is incorrect, inasmuch as we succeeded in establishing beyond all doubt the presence in the oil of both d-terpineol (m. p. 35°) and of geraniol. Judging by the odour of the first runnings, however, it must be admitted that methyl heptenone appeared to be absent. We found the oil under examination to possess the following constants: $d_{15°}$ 0,8786, α_D — 12° 29′, sap. no. 4,2 acid no. about 1, soluble in 2 vols. of 70 per cent alcohol.

The oil fractionated by us had been saponified with alcoholic potash from which the alcohol had been removed by distillation by water vapour. Apart from a small quantity of first runnings, the bulk of the oil passed over between 68 and 95° (6 to 7 mm. press.). The fractions with b. p. 68 to 75° containing the linalool were left out of account. For the determination of the terpineol we used a portion of the oil which, after repeated fractionation, passed over between 83 and 88° (7 mm. press.). The mere odour of this showed the presence of terpineol. When inoculated the cooled fraction solidified completely. The crystals, pressed out on porous tiles, melted at 35° and, in their re-melted state, had an optical rotation α_D + 18° 6′, which proved them to consist of d-terpineol. The phenyl-urethane obtained from them after treatment with carbanile had, as was expected, the m. p. 111 to 112°. In order to prove the presence of geraniol, a fraction with a b. p. of from 90 to 93° (6 m. m. press.) was heated for several hours on the water bath in benzene solution with phthalic anhydride. From the sodium salt solution of the resulting phthalic ester acid there separated upon saponification and simultaneous steam distillation, an oil with an unmistakable geraniol-like odour. This passed over at from 91 to 92° (5 mm. pressure) and at 227 to 228° under atmospheric pressure and was recognized as geraniol by its specific gravity ($d_{15°}$ 0,8820), its optical inactivity, and its odour, as well as by the diphenyl urethane (m. p. 80 to 81,5°). The terpineol content of the oil did not exceed 5 %, nor the geraniol content 1 %.

Oil of Lovage root, own distillation. After a long interval we have this year again distilled two parcels of oil of lovage from different highly developed roots, one parcel being obtained from fresh Thuringian root of the second year's growth and another from fresh root of the first season, of our own growth. In spite of the difference in the age of the material used, the oils show only unimportant differences in their properties, and a mere enumeration of their constants will therefore be sufficient: —

	Yield	$d_{15°}$	α_D	$n_{D\,20°}$	Acid no.	Ester no.	Ester no. after acet.	Solubility in 80 p. c. alc.
I. Fresh Miltitz root, 1st year	0,22 %	1,0310	+ 1° 30′	1,55148	5,8	223,5	—	in 2 vols. and more
II. Fresh Thuringian root, 2nd year	0,55 %	1,0326	+ 0° 46′	1,54944	6,1	224,5	227,8	in 2,5 vol. and more

From the but slight increase in the sap. no. after acetylation of the oil as compared with the original sap. no. we may infer that, besides the esterified alcohol, practically no free alcohol is present.

Matico Oil. We observe from a note by G. Weigel in the *Pharmazeutische Zentralhalle*[1]) that there have recently appeared in commerce matico leaves from *Piper Mandoni* D. C. which differ in important particulars from the well-known variety of the drug. They attain a length of from 18 to 20 cm., and even up to 25 cm., and mostly measure from 12 to 15 cm., but often as much as 20 cm., in width. The stalk is strong and very hairy, and the leaf is less acutely pointed than that of the familiar species and is of an oval-ovate or reversed heart shape. On the other hand, genuine matico leaves from *Piper angustifolium* Ruiz et Pavon are narrow and lanceolate, about 15 cm. long and only 4 cm. broad.

We procured a parcel of the *Piper Mandoni* leaves for distilling purposes and obtained from them about 0,8 % of a brownish oil, with a balsamic odour and with the following constants: $d_{15°}$ 0,9360, α_D + 1° 5′, $n_{D\,20°}$ 1,49704, sap. no. 1,8, ester no. 5,1, ester no. after acetylation 46,7, soluble in 6 vols. and more of 70 per cent. alcohol.

Oil of Monarda fistulosa. E. Kremers, in collaboration with N. Wakeman[2]), has made experiments in the quantitative determination of the oxidase which occurs in the leaves of *Monarda fistulosa*, and which converts into thymoquinone the hydrothymoquinone contained in this plant[3]), and the two investigators, in connection with these experiments, have made researches on both these combinations. We will only specially mention here that thymoquinone, dissolved in alcohol or limonene, was reduced to thymo-quinohydrone or hydrothymoquinone; for the rest a reference to the original paper must suffice.

Mustard Oil, genuine. We are just now engaged in working up a large parcel of exquisite material and shall shortly be able to replenish our supplies. At the moment we have not yet been able

[1]) Pharm. Zentralhalle **49** (1908), 974.
[2]) Pharm. Review **26** (1908), 314, 329, 364.
[3]) Comp. Report October **1904**, 58.

to cast up our cost price, but we can state even now that no reduction in the quotation is to be thought of, for we are already satisfied with the barest imaginable margin of profit.

Myrtle Oil. Although the oils of myrtle found in commerce are almost exclusively of French and Spanish origin, we have had frequent opportunity, of late years, of investigating oils from other sources, especially from Corsica, Asia Minor and Syria. As a matter of general interest we record below the constants of such oils: —

Oil from	$d_{15°}$	α_D	$n_{D20°}$	Acid no.	Ester no.	Ester no. after acet.	Solubility
Corsica . . .	0,8828	+ 26° 46′	1,46644	1,0	13,0	30,2	in 2,5 vol. 90 p. c. alc.
	0,8868	+ 23° 15′	1,46911	1,6	17,1	38,5	„ 0,8 „
Syria	0,8930	+ 14° 30′	—	1,9	20,3	72,0	„ 5,0 „ 80 p. c. alc.
	0,8985	+ 11°	1,46417	—	26,6	70,7	„ 1,0 „
Asia Minor .	0,9138	+ 10° 42′	1,46704	1,5	39,4	94,9	„ 0,9 „

In connection herewith we may mention that in the course of our investigations we have also observed small differences in the constants of Spanish and French oils. These are shown in the subjoined table:

	$d_{15°}$	α_D	$n_{D20°}$	Acid no.	Ester no.	Ester no. after acet.	Solubility
Spanish oils	0,913 to 0,924	+ 22° to + 25° 20′	1,467 to 1,470	up to 1,7	68 to 83	103 to 117	in 1 to 2, rarely up to 5 vol. 80 p. c. alc.
French oils	0,890 to 0,904	+ 15° to + 23°	1,465 to 1,468	up to 1,5	19 to 28	38 to 56	in 0,5 vol. 90 p. c. alc., the majority in 5 to 10 vol. 80 p. c. alc.

Neroli Oil. In spite of the unfavourable weather (among the features of which are hail and snow storms), which has prevailed in the South of France during the past month, the orange trees have only suffered very slightly, and from their appearance it is hoped that the crop will be a middling one. The cold weather has greatly retarded the young buds, and the experience of past seasons shows that when the blossoming-period commences late it is comparatively short and consequently never yields a very abundant crop. In any case it may be anticipated that the prices of flowers will be somewhat lower than in 1908 and, presupposing that no continuance of bad weather nullifies all prophecies, neroli oil is also likely to be offered at somewhat more advantageous rates.

A business-friend at Besançon has sent us, by way of a curiosity, an oil of neroli distilled from orange-flowers gathered in the locality. The small sample was of a bright brown colour and possessed a quite agreeable, although not very fine aroma. Apart from a somewhat high acid no., its constants were approximately normal: $d_{15°}$ 0,8780, $\alpha_D + 7° 15'$, acid no. 6,1, ester no. 58,4 soluble in 1,3 vol. of 80 per cent alcohol. When more alcohol was added, cloudiness ensued and paraffin was separated.

Nutmeg Oil. In the course of their investigations in the toxic effects of nutmegs (referred to on page 114 of the present Report), F. B. Power and A. H. Salway[1]) also deal with the requirements attached to essential oil of nutmeg in certain Pharmacopœias. Of this part of the paper we will only say that Power and Salway rightly regard it as illogical that the German Pharmacopœia should designate essential oil from nutmegs by the name of *Oleum Macidis*, since by mace oil is understood the oil of the nutmeg flower and since the identity of the two oils has not been established. While the American Pharmacopœia originally required the oil to possess a specific gravity of 0,862 to 0,910 at 25°[2]) the Supplement to that Pharmacopœia demands 0,884 to 0,924[3]). Power and Salway assume this to be a mistake for 0,864. The requirement of the U. S. Ph. (obviously taken from the British Pharmacopœia), that from 2 to 3 cc. of nutmeg oil must leave no crystalline residue upon evaporation is regarded as unpractical, as normal distillates will often fail to satisfy this demand, because the fractions of the oil with the highest b. p. contain myristic acid. Hence, an oil which unconditionally conforms to the requirements of the U. S. Ph. would consist only of the fractions possessing the lower boiling points.

Orris Oil. We have received the following report from our correspondents: —

At the time of our October report on Florentine orris-root, the price was 62 to 63 marks cif. Hamburg for pickings, and 52 to 53 marks cif. Hamburg for seconds. At that time we estimated the new crop at about 400 tons, but as, owing to the favourable weather conditions prevailing, the supplies came in during a longer period than usual, the actual crop amounts to about 500 tons.

Add to this the remainder of old stocks at the end of September 1908 . . . . . „ 515 „

The total supply available for the new campaign was therefore . . . . . about 1015 tons.

The shipments from the end of September 1908 to the end of February 1909 amounted to . . . . . „ 265 „

leaving available at present (1st March 1909) . . . . . about 750 tons.

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[1]) Americ. Journ. Pharm. **80** (1908), 568.
[2]) Report April **1906**, 75.
[3]) Report October **1907**, 102.

The exports from the beginning of October up to the end of February (about 265 tons) cannot be called heavy, but just recently numerous orders have been received, particularly from France. Moreover, the scanty yield of the crop in the district of Verona (according to our latest computations it amounted only to about 70 tons, compared with a maximum yield of 600 tons a few years ago), has also influence on the Florentine market. Numerous orders have come in for the latter variety, as a result of which, along with the new crop, the still remaining stocks of Veronese orris root have been exhausted, excepting a small quantity which is in firm hands. This fact has further strengthened the position. Veronese orris of the quality known as "mercantile" was purchasable in October for 35 marks, whereas now the parity of 43 marks cif. Hamburg is being paid. Hence a speculative movement has developed locally in Florentine orris root, and the orders which are coming in are encouraging the dealers and speculators to further purchases, with the result that we are at present compelled to quote 64 marks for Florentine orris in pickings, and 54 marks for seconds, both cif. Hamburg. It will of course depend upon the future demand whether these prices will be maintained or perhaps advance still further. We have already previously stated that of about 515 tons of old stock, about 100 tons are worm-eaten, and it appears that since we wrote the proportion of worm-eaten root has become still larger, for which reason great care is necessary in buying. The yield of the last seven crops has been as follows: —

1902 . .	about	1000	tons,
1903 . .	„	750	„
1904 . .	„	670	„
1905 . .	„	850	„
1906 . .	„	800	„
1907 . .	„	500	„
1908 . .	„	500	„
Total	about	5070	tons,
Average	about	725	tons.

On the other hand, the average annual exports during the past six years, according to our October report, amounted to about 692 tons. In case, therefore, the next succeeding crops should again average only about 500 tons, or even less, as appears likely owing to the reduced planting, this shortage, judging from the statistical position of the article, might easily start a rise in prices, unless the consumption of orris root should fall off owing to the cheapness of ionone, as to which we are, however, unable to form an opinion.

In connection with the concluding sentence of the above review, we may state that, in our opinion, it is true that the competition of cheap violet-scents makes itself felt by restricting business in orris oil, and that he who would build his plans upon a brisker demand during the next months would probably make a miscalculation. Moreover, it is to be remembered that on March 1st the available stock amounted to full 750 tons, that is to say more than an average season's production. Even a restriction of planting is therefore unlikely to have a stiffening effect upon the market position in the near future.

Parsley Oil. As the apiol content of German oils differs from that of French oils of parsley[1]), H. Thoms[2]) had intended to

[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 548.
[2]) Berl. Berichte **36** (1903), 3451; Report April **1904**, 67.

determine by cultivation experiments whether external conditions, such as mode of cultivation, climate etc., were of influence in causing this difference. The results of his experiments, which have now been published[1]), are interesting in several respects. Of the French seed, which was supplied by us, a portion was immediately distilled (sample no. 1), while the rest was sown at Dahlem in Germany in the spring of 1904. The fruit of this, gathered in the autumn of 1905, was distilled in February 1906 (sample no. 2). As the following table shows, the differences in the composition of the two oils are only slight, but it must be borne in mind that important influences would only be perceptible after repeated cultivation: —

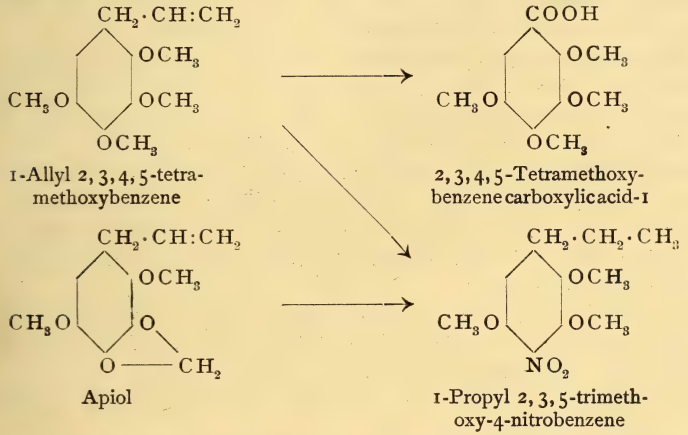
	Sample 1	Sample 2
$d_{15°}$	1,03	1,07
Terpene content	about 5 %	about 5 %
Acid mixture (chiefly palmitic acid)	0,1746 %	0,876 %
Phenols	0,184 %	2,51 %
Principal fractions at 15 mm. pressure		
a) 160 to 165°	28 %	25 %
b) 165 to 170°	47 %	35 %

The determinations of carbon, hydrogen, and methoxyl showed that in both oils the principal fractions possessed approximately the same composition. In all the four fractions the presence of apiol could be detected, and by brominating, myristicin was found in the form of dibromo myristicin dibromide, while the high values obtained for the methoxyl content further indicated the presence of a phenol ether still richer in methoxyl. In order to determine the character of the last-named body, the fraction was first treated with alcoholic potash and afterwards reduced with sodium in alcoholic solution. But neither from the hydrated phenol which had been obtained by this process (b. p. 156 to 160° at 17 mm. pressure) nor from its methylation product (b. p. 160 to 165° at 19 mm. pressure) could any solid bodies be isolated by cooling. Both substances, however, yielded a nitro product melting at 65°, which proved to be identical with the 1-propyl 2, 3, 5-trimethoxy 4-nitrobenzene already previously obtained from apiol[2]). Oxidation of the fractions with permanganate, however, threw some light upon the character of the phenol ether in question, for besides yielding myristicinic and apiolic acids, this process resulted in the formation, as the principal product, of 2, 3, 4, 5-tetramethoxy benzene carboxylic acid-1, which had already been previously obtained by Bignami and Testoni[3]) by the oxidation of a fraction of parsley oil. Finally Thoms succeeded, by cooling the fractions with solid carbonic acid, in isolating the phenol-ether itself in solid form. Among its constants the following may be

[1]) Berl. Berichte **41** (1908), 2753.
[2]) Berl. Berichte **36** (1903), 1714; Report October **1903**, 100.
[3]) Gazz. chim. ital. **30** (1900), I. 240; Report October **1900**, 48.

mentioned: m. p. 25°, $d_{25°}$ 1,087, $n_{D25°}$ 1,51462, mol. refr. found 65,7, calculated 64,77. The pure body also was converted into the acid (m. p. 87°) by oxidation and into the nitrated compound (m. p. 65°) by reduction and subsequent nitration. These facts, together with its behaviour towards alcoholic potash, phloroglucinol and hydrochloric acid, picric acid, or hydrochloric acid, as well as the values ascertained for refraction and dispersion, made it possible to determine its nature as 1-allyl 2,3,4,5-tetramethoxybenzene, a body which has not previously been found in essential oils.

The following formulæ exhibit the connection existing between the combinations in question: —



1-Allyl 2,3,4,5-tetramethoxybenzene

2,3,4,5-Tetramethoxybenzene carboxylic acid-1

Apiol

1-Propyl 2,3,5-trimethoxy-4-nitrobenzene

Patchouli Oil. The value of this oil, which is such an indispensable article in the perfumery trade, has remained entirely unaltered since last October. It has all along been difficult to procure suitable material for distilling purposes, and in face of the keen competition of the cheap, albeit generally thoroughly bad, Indian distillate, the profit on patchouli oil of our own manufacture is being so much reduced that important transactions can only be effected in the case of customers who are really connoisseurs.

In our last Report[1]) we published particulars of the examination of a series of patchouli oils which had been sent to us by Dr. de Jong. Roure-Bertrand Fils have obtained a similar collection from Buitenzorg, and they communicate the result of their investigations on these in their *Berichte*[2]). With one exception these results tally with those obtained by us. The exception is that Messrs. Roure-Bertrand

[1]) Report November **1908**, 95.

[2]) Berichte of Roure-Bertrand Fils, October **1908**, 27.

Fils found one of the two oils prepared from fresh Java leaves to possess the following constants: $d_{15°}$ 0,9112, α_D + 0° 52′, sap. no. 4,1, soluble in 8,5 vols. and more of 90 per cent. alcohol. In our case, both these oils were found to be lævorotatory, to have a higher specific gravity and to be more readily soluble.

From a paper read in Berlin by Prof. Preuss[1]) we observe that experimental distillations have been made of wild patchouli plants from New Guinea. The oil yield was 3,75 % and the experiment was so promising that it is intended to commence the cultivation of patchouli there. A similar specimen-distillate examined by us showed the following constants: $d_{15°}$ 0,9847, α_D — 58° 10′, sap. no. 1,8, ester no. 8,4, soluble in 0,4 vol. and more of 90 % alcohol.

Peppermint Oil, American. During the last six months the market has offered little of interest, and the prices showed a falling tendency, as the demand has not been proportionate to the supply.

The yield of the 1908 crop was smaller than that of the two preceding years, but the existence of sufficiently large stocks held over from 1906 and 1907 more than compensated for the reduction, and even if in the coming season there should be a further restriction in the laying down of new plantations, there will yet remain quite sufficient oil for disposal.

The farmers are to a large extent losing their interest in cultivation, and it is becoming more difficult every season to find special qualities, as not sufficient new plantations are laid down, and the old plantations, owing to the low market prices, are not attended to and cleaned with sufficient care.

Our stock for the next months to come has been excellently assorted by timely purchases, and we believe that at the prices now prevailing, which are still low, we are justified in advising our clients to supply their wants quickly and plentifully.

Peppermint Oil, French. In their last *Bericht* Roure-Bertrand Fils[2]) make some statements with regard to observations on peppermint oils from Grasse, which we here reproduce shortly. Two oils distilled in 1907 and 1908 behaved as follows: —

	1907		1908	
	Crude	Rectified	Crude	Rectified
$d_{15°}$	0,9210	0,9198	0,9156	0,9159
α_D	— 13° 4′	— 17° 6′	— 15° 28′	— 16° 50′
Menthyl acetate . .	13,5 %	13,7 %	15,4 %	13,3 %
Total menthol . .	49,8 %	53,5 %	52,2 %	54,9 %

[1]) Berichte d. deutsch. pharm. Ges. **19** (1909), 25.
[2]) Berichte of Roure-Bertrand Fils, October **1908**, 23.

In referring to the differences between Grasse peppermint oil and that of other origin, Roure-Bertrand Fils also call attention to the fact that the Grasse variety would not be admitted by most Pharmacopœias. If the firm should conclude from this that the requirements of the Pharmacopœias have been laid down "without sufficient technical knowledge", such a judgment must be regarded as somewhat too severe. Outside France, French oil does not enter into commerce at all, and it is therefore not surprising if the Pharmacopœias have not paid special attention to it.

As a special peculiarity of the Grasse oil, Roure-Bertrand Fils mention its behaviour in a freezing mixture. Even when cooled down to — 17° it was impossible to bring the oil to congealing point, even after inoculating it with menthol. It is hoped that the intended examination of the alcoholic constituents will explain this behaviour of the oil.

To the foregoing we would add that in the case of the highly esteemed English and Saxon oils also crystalline separations frequently only take place after the oils have remained for a long time in the freezing mixture; hence the quantity of crystallisable menthol differs altogether in the oils of various origin, and is not a direct measure of their value. At the same time we refer to our own communications on South French peppermint oils[1]), which partly behaved similarly to to those examined by Roure-Bertrand Fils. We may further place on record here an observation which we have made concerning the rapid resinification of two oils distilled by ourselves in Barrême. Both oils were examined some weeks after distillation, and at first behaved as follows: —

1. $d_{15°}$ 0,9184; α_D — 10°44′; mthl. as ester 12,0 %; total mthl. 50,2 % } Sol. in 1,1 vol. 80 p.c. alc.; with more than 2,5 to 3 vol. pronounc. opalescence.
2. $d_{15°}$ 0,9273; α_D — 10°56′; „ „ „ 14,8 %; „ 54,7 % }

Accidentally the specific gravity was again determined a fortnight afterwards, on which occasion a considerable increase in weight was ascertained. Two following observations, made at intervals of a fortnight each, showed a further increase, which is indicated in the following table: —

	Originally	After a fortnight	After 4 weeks	After 6 weeks
Oil 1.	$d_{15°}$ 0,9184	0,9191	0,9224	0,9292
„ 2.	$d_{15°}$ 0,9273	0,9291	0,9322	0,9380

The reason for this is to be found in the fact that the herb had been worked up while it was still quite green. In such a state, readily resinifying constituents pass into the oil, which, if the herb

[1]) Report April **1905**, 62; October **1906**, 58. The places of origin of the oils were Cannes, Cagnes, Castellane, and Barrême.

has been previously dried, are quickly converted by the oxygen of the atmosphere into non-volatile resins, and thus made harmless. As such constituents make the oil entirely useless in certain conditions, it is advisable not to distil the fresh herb, but only the dry, or at any rate the faded, herb. The same applies to many other distilling materials, such as for instance lovage root.

Peppermint Oil, Japanese. So far as the final result of the last harvest can be ascertained, the total output will fall far below the quantity mentioned in our last Report. In London, for instance, it is asserted that at most 2000 cases have been produced, of which one half is said to consist of oil and the other of menthol. Unfortunately no authentic statistics are available on the present occasion.

Business in oil and menthol has been just as unsatisfactory in the course of the last half-year as in the period covered by our last Report, and we scarcely believe that better times are to be hoped for shortly. On the one hand the prices of American oil, which continue to be very depressed, are an obstacle to a revival of the Japanese market, and secondly there continue to be in existence considerable old stocks, both here and in Japan, which also help to weigh upon the market. For many months past those who are interested in the matter in Japan have been vainly endeavouring, by holding the prices firmly, to bring about a renewed interest in it. In spite of all their efforts, consumers only buy for actual requirements. Recently, even a decided slackening of the market has been observed.

Peppermint Oil, Saxon. It would be premature at the present time to express an opinion on the prospects of the coming season's crop, for only when the shoots are beginning to form will it become clear whether the unusually late winter, and particularly the cold weather of the last few months of the past year, which was not accompanied by snow, have or have not exercised an injurious effect upon our cultivations.

Petitgrain Oil, Paraguay. Depressed by the considerable supplies as well as by lower offers for later shipments, the prices again began to move towards a normal level as far back as in the late autumn, and they have now reached a range where the oil promises again to become of interest to consumers. It is, however, more than doubtful whether such low prices as those of former years will return, because it is said that the conditions of manufacture in the country of origin have become very difficult.

Pine-needle Oils. Owing to the weakening of the demand, somewhat large quantities of extra-fine oil from fir cones accumulated, so that it even became possible to effect a slight reduction in

the price. Unfortunately the supplies of the Thuringian distillate, already referred to in our last Report, are very insignificant, for which reason it has not yet been feasible to bring back the price to a normal figure. It is to be hoped that the Thuringian producers will not fail to take advantage of the situation this year, so that it may become possible ere long to leave the Swiss producers, with their exaggerated demands, severely alone. The scarcity of the oil has of course been the signal for a number of firms to endow the international market with all sorts and descriptions of inferior compounds, attracting attention, to be sure, because of their low prices, but wanting both as to the constants and the delicate odour of the genuine oil. Any consumer may prepare such products much more cheaply himself by having recourse to Siberian pine-needle oil. The last-named article is steadily gaining favour among users who are compelled to employ a low-priced oil for the purpose of scenting varnishes, lubricants, dressings, greases, etc. There has been no lack of pine oil from *Abies pectinata* D. C. and *Pinus pumilio* Haenke, and we are justified in asserting that the difficulties which were formerly experienced in procuring these varieties are now probably removed for good.

We avail ourselves of this opportunity to point out that the designation *Oleum Pini silvestris*, which is frequently applied to oil from fir cones (templin oil, *Oleum templini*) is quite a misnomer, and gives rise to constant confusion, for which reason it is desirable that retail-traders as well as others should gradually accustom themselves to accuracy in referring to the oil. We again emphatically lay stress upon the fact that although *Oleum Pini silvestris,* that is to say, oil made from the needles of the common pine (*Pinus silvestris* L.), has often been distilled on experimental scale, yet, owing to its somewhat disagreeable odour, it has never acquired popularity, and has therefore never been manufactured on a large scale. Hence, as we have already stated on a previous occasion[1]), it plays no part at all as a commercial article.

The constant confusion of this oil with oil from fir cones (*Abies pectinata D. C.*) has been the cause why genuine oil from pine-needles, notwithstanding that is unobtainable commercially, has nevertheless been incorporated into Pharmacopœias, for example in the Russian Pharmacopœia and in the Supplement to the 4th Edition of the German Pharmacopœia. At the time when we reviewed these books[2]) we pointed out that it was quite out of place to make such an oil official, seeing that it was unobtainable. In order to obviate useless correspondence,

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[1]) Gildemeister and Hoffmann, *The Volatile Oils*, p. 258.
[2]) Report October **1904**, 95; October **1906**, 94.

we repeat this statement here, and at the same time we place it on record that the article which goes by the name of *Oleum Pini silvestris* in commerce, is really oil from cones of *Abies pectinata D. C.* (*Oleum templinum*). In the existing conditions it would certainly be better if the designation "*Oleum Pini silvestris*" were to disappear from the commercial vocabulary altogether, and were exclusively reserved to the real oil from pine-needles.

While working up a large parcel of oil from cones of *Abies pectinata D. C.* for l-limonene, we were able to prove definitely the presence of borneol in this oil. Bertram and Walbaum[1]), while examining this oil, had already discovered an ester, but they were unable to determine its character, as it only occurs in small proportions in the oil. They surmised that this ester represented bornyl acetate, because this substance is a constituent of almost all pine-needle oils.

The oil worked up by us, and referred to above, possessed the following constants: $d_{15°}$ 0,8556, $n_{D20°}$ 1,47246, α_D — 76° 30′, ester no. 5,3. The oil was freed from terpenes by fractional distillation and saponified. The resultant alcohols were found to boil between 190 and 225°. The principal fraction (b. p. 205 to 215°) was heated with phthalic anhydride and the acid ester formed was recrystallised from alcohol. The m. p. (164°) is that of the acid phthalic ester of borneol. Owing to the smallness of the sample available it was impossible to identify the borneol by other combinations. In addition, there appeared to be present in the oil, another alcohol (b. p. 190 to 197°; $d_{15°}$ 0,9013), and a sesquiterpene.

From Siberian pine needle oil, P. G. Golubeff[2]) obtained by distillation, after heating the oil to 50 to 60° with a mixture of sulphuric and acetic acids and saponifying with alcoholic potash solution, a solid, inactive camphene (m. p. 47 to 48°; b. p. 157 to 158°). When hydrated, this camphene, like the l-camphene obtained from the crude oil of the Siberian pine, yielded i-isoborneol, which was convertible into i-campher (m. p. 178 to 179°, b. p. 204°) by means of nitric acid or permanganate.

From the needles of the Australian pine tree *Callitris glauca* R. T. Baker and H. G. Smith[3]) obtained 0,6 % of a volatile oil with a content of about 12 to 16 % bornyl acetate and geranyl acetate. The constants of the crude oil moved within the following limits: d 0,8631 to 0,8782, α_D + 22,7 to + 31,3°, n_D 1,4747 to 1,4779.

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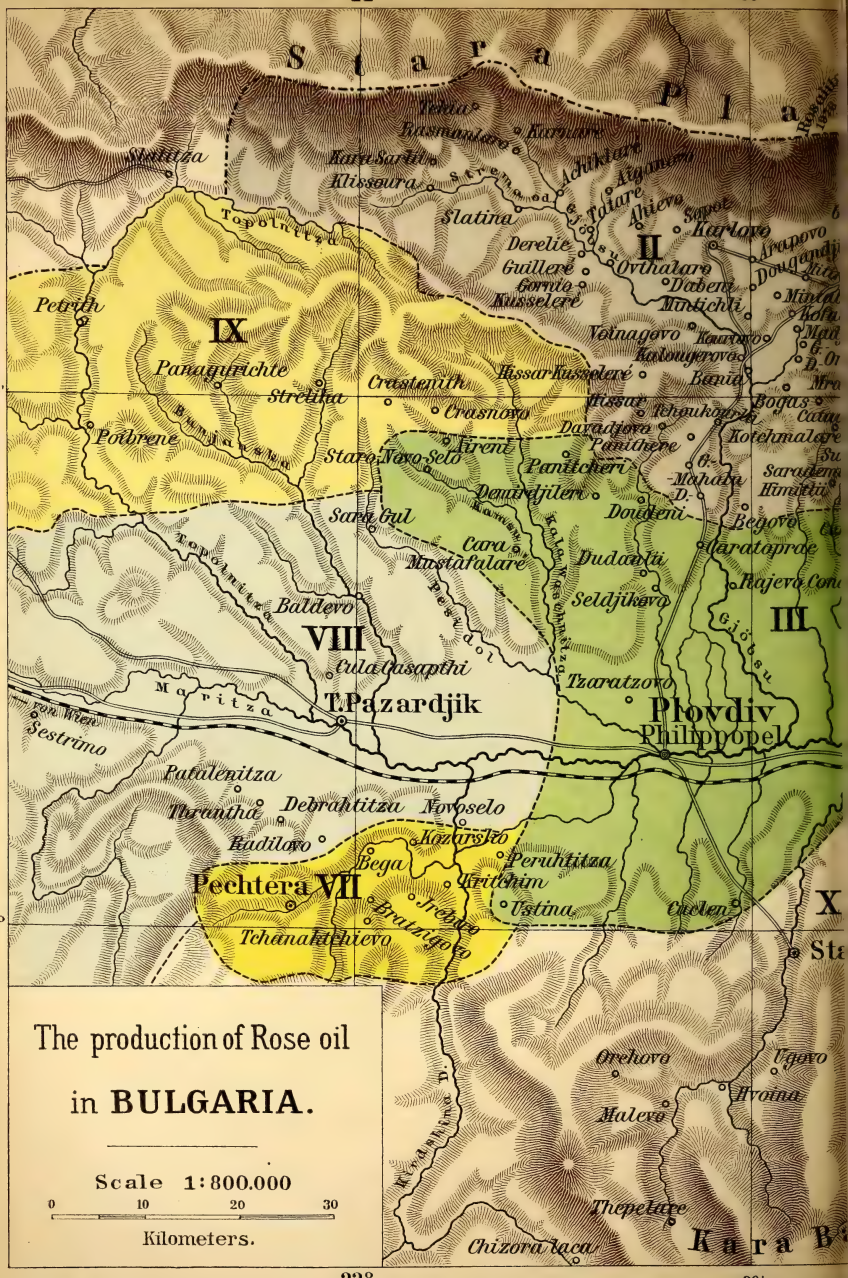
[1]) Arch. der Pharm. **231** (1893), 293; Report April **1893**, 55.

[2]) Meeting of the Chem. Section of the Russian phys. chem. Soc., May 8/21, 1908. According to Chem. Ztg. **32** (1908), 922.

[3]) Roy. Soc. N. S. Wales. Abstract of Proceedings, Aug. 1908, iii. Quoted from Journ. Soc. chem. Industry **27** (1908), 1039.



The production of Rose oil

in **BULGARIA.**

Scale 1:800.000

0 10 20 30

Kilometers.

23°
30'
42°
Districts:
I Kazanlik
II Karlovo
III Plovdiv
IV Nova-Zagora
V Stara-Zagora
VI Tchirpan
VII Pechtera
VIII Pazardjik
IX Panagurichte
X Stanimaka
Kazanlik
Tchirpan
S.-Zagora
N.-Zagora
Chaskovo
Uzun
Ahijevo
Maritza
nach Konstantinopel

22°
30'
23°
30'
Stara Planina (Balkan)
Districts:
I Kazanlik
II Karlovo
III Plovdiv
IV Nova-Zagora
V Stara-Zagora
VI Tchirpan
VII Pechtera
VIII Pazardjik
IX Panagurichte
X Stanimaka
The production of Rose oil in BULGARIA.
Scale 1:800.000
0 10 20 30
Kilometers.
Kara Balkan
Rhodope Mts.
Kazanlik
Karlovo
Orhaniye
Kalofer
Shipka Pass
Gabarevo
Tarnitschane
Dolnoudjane
Mintablii
Kehlulare
Martjare
Omarobas
Kazandjik
Yeni Zagra
Nova Machala
Kaloyerovo
Bania
Mratchinik
Adjar
Bogas
Catadjica aje
Koretamalare
Saadtlie
Babek
Hamzalar
Kolatchevo
Sakartia
Sadaklii
Brezovo
Mestim
Derelie
Evdjivlere
Echerren
Tchirpan
Assarlarovo
Thicarlia
Enihieri
Shahovo
Ahmatovo
Uzun
Chaskovo
Ograzden Mts.
Rhodope Mts.
Pechtera
Tchanakdjievo
Ustina
Perushtitza
Bega
Brezhani
Ivrdjam
Cocleu
Stanimaka
Ortchalare
Dabeni
Mandschi
Yelnagovo
Kartsovo
Kalougerovo
Hissar
Tchaukoglu
Daradjova
Panithere
Panitcheri
Demirdjileri
Doudeni
Cara Mustafalare
Dudaclu
Seldjikovo
Begovo
Cemarlare
Ratcheva Cenaee
Baldevo
Cula Dasphli
T. Pazardjik
Plovdiv
Philippopel
Tzaratzovo
Patalenitza
Ihranlia
Debrahtitza
Novoselo
Kadilovo
Kozarsko
Strelcha
Panagurichte
Potkrae
Stara Novo Selo
Sarh Gul
Topolnitza
Maritza
Sestrimo
Arda
Rhodope Mts.
Ihtiman
Dolna Banya
Kostenetz
Samokov
Dupnitza
Rila Mts.
Rhodope Mts.
Orchovo
Ugovo
Irvina
Malcva
Thepelare
Chizovaraca
Rhodope Mts.
Schimmel & Co.'s Semi annual Report, April/May 1909.

The following terpenes, viz., d-pinene, d-limonene, and dipentene, were found to occur in the oil. The borneol and its acetate contained in the oil were dextrorotatory.

Upon distilling the wood the authors obtained a thick oil containing guajacol and a new phenol "callitrol".

The sandarach resin yielded by this variety of tree was inferior to that from *Callitris calcarata.*

Rose Oil, Bulgarian. In order to afford a better understanding of the tables relating to the production of rose oil [1]) which we published in our last Report, we now present our readers with a map of the districts where rose oil is produced, giving a survey of this interesting region which has been so frequently alluded to in former Reports. In this case also, we are indebted for the data upon which our information is based to Messrs. S. Seraphimoff & Co., of Kazanlik.

Transactions in rose oil have naturally suffered during the past half year under the general depression of trade, and if notwithstanding this prices have remained unchanged, this may be ascribed in the first place to the fact that at the very beginning of the last crop an extremely lively interest for the article was shown on all sides. Any oil which was not sold firm for delivery passed into the hands of wealthy exporters, who were in a position to await the demand without depressing the market with their stocks. It will be clear, without further explanation, that these firms have not experienced much satisfaction from the transactions in rose oil during the past six months, for experience shows that when business is dull valuable articles are those which excite the least desire to purchase.

Roure-Bertrand Fils[2]) report on an oil from white Bulgarian roses. It possessed the following constants: $d_{15°}$ 0,8723, α_D — 2° 54′, ester no. 11,14, ester no. after acetylation 222,44, corresponding to 74,44 per cent. of alcohols of the formula $C_{10}H_{20}O$. The oil is soluble, with strongly marked separation of paraffin, in 1 vol. of 90 per cent. alcohol. At + 14° it is solid, but at 20° it liquefies completely. Its odour is much less delicate and persistent than that of the oil from red roses, and Roure-Bertrand Fils therefore advise that the latter only should be used for distilling purposes. The fact that the white roses are the less valuable variety is also the reason which, in 1906, induced the Chamber of Commerce of Philippopolis to urge upon the distillers the advisability of abandoning the cultivation of the white roses[3]).

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[1]) Report November **1908**, 105 to 107.
[2]) Berichte of Roure-Bertrand Fils, October **1908**, 28.
[3]) Comp. Report October **1906**, 66.

Rosemary Oil. The prices for French as well as for Dalmatian oil have become decidedly firmer in the course of the last few months, and in the districts of production the supplies are beginning to lessen. On account of the low value, the oil has gained numerous new consumers, especially the French kind, and it is likely that the market may shortly acquire increased firmness.

We have already previously referred to the observations of Birckenstock[1]) with regard to the changes, according to the season of the year, in the composition of oil of *Rosmarinus officinalis* L.[2]).

Rue Oil. We have already on a previous occasion referred to an article by Birckenstock[3]) on the effect of the season upon the oil contained in Algerian rue[4]).

From Corfu we received offers of two oils of sage, which possibly were not derived from *Salvia officinalis* L., because, in contradistinction to ordinary oil of sage, they were lævorotatory. The odour also was different, thujone being less perceptible. The constants of the pale yellow, almost colourless distillates, were as follows: —

$d_{15°}$ 0,9153, α_D — 15° 14′, acid no. 0,5, ester no. 9,0
„ 0,9132, „ — 15° 5′, „ „ 0,5, „ „ 10,6

The oils were soluble in 1,3 vols. of 80 per cent. alcohol and more. Of 70 per cent. alcohol, about 25 vols. were needed to effect solution.

Sage Oil. In a short paper on the present state of research in sage oil, T. F. Harvey[5]) refers to investigations by A. Tompkin, who has examined one Spanish and four Dalmatian oils. The first-named possessed the following constants: d 0,9053, α_D + 9,60°, $n_{D20°}$ 1,4619, acid no. 0,6, ester no. 17,2, total borneol 15,2 %; soluble in 2 vol. of 80 per cent. alcohol. The values of the Dalmatian oils moved within the following limits: d 0,921 to 0,9253, α_D + 9,93° to + 13,62°, $n_{D20°}$ 1,4618 to 1,4645, acid no. 1,3 to 2,2, ester no. 6,7 to 8,5, total borneol 9,5 to 14,8 %, soluble in 1 and more vol. alcohol. The oils boiled chiefly between 170 and 220°; below 170° only 2 to 3 % passed over, between 170 and 200° 55 to 65 %, and between 200 and 220° 21 to 31 %. The corresponding fractions of the Spanish oil were 13,64 and 10 %. We have made frequent communications about oil of sage in our recent Reports, to which we may here refer[6]).

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[1]) Journ. de la Parfumerie et Savonnerie **21** (1908), 231.
[2]) Report October **1906**, 69.
[3]) Journ. de la Parfumerie et Savonnerie **21** (1908), 231.
[4]) Report October **1906**, 70.
[5]) Chemist and Druggist **73** (1908), 393.
[6]) Report April **1907**, 90; October **1907**, 79; April **1908**, 89.

Sandalwood Oil, East Indian. About 10 per cent. less wood was placed on sale during the last auctions than in 1907. As was to be expected, little desire for buying was shown, and as, moreover, the Government at first fixed limits which were entirely out of the question, not much more than half of the quantity offered was sold, mostly to native dealers. Further details with regard to the prices as compared with the previous year may be gleaned from the table on page 84.

Altogether about 991 tons remained unsold, and nothing was now for it but to endeavour to obtain limits. This, however, also resulted only partly in business, as the exporters kept themselves very much aloof in consequence of the depressed state of trade in Europe and the United States, and as the offers made ranged very considerably below the ideas of prices entertained by the Government. Finally, however, a few important transactions were concluded at low quotations, and perhaps those concerned in India will learn from the results of the present season the lesson that it is not advisable to ride the high horse too much at the very beginning of the auctions.

The prices of East Indian sandalwood oil remained unchanged last winter, and the end of the continued cutting of prices has been that certain firms have been compelled to vacate the field. In this article only the manufacture on a true wholesale scale, with the most modern and rational appliances — such as are to be found in our works — can be made to pay. In the extension of our factory, which has recently been completed, we have had special regard to the considerable enlargement of our plant for distilling sandalwood, and we are therefore now equipped to meet successfully with all competition.

K. Bode[1]) makes a communication on the constituents and properties of East Indian Sandalwood oil. His short paper passes in review our present knowledge of the production, properties and composition of sandalwood oil, and should be of interest to all who wish to make themselves rapidly acquainted with what is best worth knowing about the article.

For the reactions of eksantalal, see Aldehydes, p. 128.

Schinus Oil. In our previous April Report[2]) we gave some particulars of two schinus oils of Mexican origin. In the meantime we have received another such oil from Mexico, the properties and constants of which are briefly recorded here: pale yellow, $d_{15°}$ 0,8492, α_D + 56° 27′, $n_{D20°}$ 1,47616. Even with absolute alcohol it only at first

[1]) Apotheker Ztg. **24** (1909), 17.
[2]) Report April **1908**, 121.

Auction	Fraserpett		Hunsur		Seringapatam		Bangalore		Hassan		Chickmagalur		Tarikere		Shimoga		Sagar		Tirthahalli	
	18./12. 1907	16./11. 1908	16./12. 1907	19./11. 1908	12./12. 1907	23./11. 1908	9./12. 1907	25./11. 1908	5./12. 1907	30./11. 1908	2./12. 1907	3./12. 1908	28./11. 1907	7./12. 1908	25./11. u. 26./11. 1907	10./12. 1908	21./11. 1907	14./12. 1908	18./11. 1907	17./12. 1908
Prices realised: —	cif d. w. p. cwt.		cif d. w. p. cwt.		cif d. w. p. cwt.		cif d. w. p. cwt.		cif d. w. p. cwt.		cif d. w. p. cwt.		cif d. w. p. cwt.		cif d. w. p. cwt.		cif d. w. p. cwt.		cif d. w. p. cwt.	
2nd Class Billets . .	—	—	—	—	58/3	—	58/6	—	57/6	—	59/6	—	58/-	55/6	—	—	—	—	—	—
3rd „ „ . .	—	—	—	57/-	59/3	55/6	—	—	—	—	59/6	—	59/6	56/-	58/6	—	54/6	—	57/-	—
Ghotla	—	—	—	56/6	—	55/3	—	—	—	—	—	—	—	—	—	—	—	—	57/6	—
Ghatbadala	54/-	55/-	52/-	51/6	52/6	50/5	53/-	—	52/6	49/6	53/3	50/-	54/6	50/6	54/-	—	51/3	—	53/3	49/3
Bagaradad	—	55/-	—	54/-	—	53/3	—	—	54/6	—	—	—	55/6	53/3	55/3	53/-	51/3	—	—	—
1st Class Roots . . .	60/3	60/-	57/-	57/6	—	—	—	—	57/6	56/6	58/6	56/-	59/-	56/6	—	—	56/6	—	58/9	—
2nd „ „ . . .	61/-	60/6	56/9	57/6	—	—	—	—	—	55/-	58/6	55/-	59/-	56/6	—	—	56/3	—	58/6	—
3rd „ „ . . .	—	60/-	—	56/6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	57/3	—
1st „ Jugpokal. .	53/3	54/-	50/-	—	51/3	—	51/3	—	—	47/6	52/3	47/-	52/6	47/-	52/- to 52/9	—	50/3	44/6 to 45/-	50/-	44/6 to 45/-
2nd „ „ „	50/6	50/9	—	—	47/3	—	—	—	—	—	48/6	44/-	49/3	—	—	44/3	48/6	43/-	49/6	—
Ain Bagar	—	55/-	—	46/-	47/3	46/-	—	—	47/9	—	47/6	—	—	—	47/6	—	—	—	46/6	—
Cheria	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	44/3	—
Ain Chilta	—	—	33/3 to 34/9	33/3	33/-	—	32/9	—	33/6	32/6	33/3	32/9	33/3	33/-	32/3	—	32/-	—	32/3	—
Hatri Chilta	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Milwa Chilta	22/6	—	22/9	20/6	22/6	19/9	23/-	—	23/-	20/6	22/6	19/9	23/6	19/9	22/9	—	23/3	19/-	22/6	19/-
Basola Bukni	—	17/-	16/3	—	16/3	—	16/3	—	16/9	—	—	15/6	—	14/6	19/-	—	19/-	—	19/-	14/6

gives a clear solution; when more than 0,7 vol. of alcohol are added, cloudiness ensues. The oil is very rich in phellandrene. Unfortunately we have not heard whether the oil is prepared from the leaves or from the fruit; the distillates from both these parts (as has been pointed out in previous Reports) being almost identical.

Snake root Oil, Canadian. Two Canadian snake root oils distilled by ourselves from *Asarum canadense* L. possessed the following constants: —

No. 1. From roots with fibres: $d_{15°}$ 0,9519, α_D — 10° 30′, $n_{D\,20°}$ 1,49987, acid. no. 4,7, ester no. 74,7, ester no. after acetylation 125,0, soluble in 2,5 vols. and more of 70 per cent. alcohol.

No. 2. From roots without fibres: $d_{15°}$ 0,9520, α_D — 10° 42′, $n_{D\,20°}$ 1,48863, acid no. 3,1, ester no. 86,1, ester no. after acetyl. 125,8, soluble in 2,3 vols. and more of 70 per cent. alcohol.

Spearmint Oil. The excitement which prevailed in this article last summer has completely subsided, and prices move within normal limits. A large part of last year's crop had been contracted for in advance, and has been used up in the manufacture of chewing-gum. Enough was left, however, to cover the remaining requirements and there are signs that during the current year also a sufficiency of oil will be available at reasonable rates. But little spearmint is nowadays cultivated in the State of New York, which is to be regretted, because the oil yielded by the New York herb was superior in quality to the oil from Michigan.

We have recently had several opportunities of examining Hungarian spearmint oils. We were informed that they had been distilled from the dry herb. Their composition is similar to that of the German and American distillates, but they differ from them in their higher carvone content, which runs up to 72% as against only about 50% in German and American oils. Corresponding with their greater carvone content the specific gravity of the Hungarian oils was also in every case higher than that of the other varieties, and their greater solubility also attracted attention. The Hungarian oils give a clear solution with 1 vol. and more of 80 per cent. alcohol, whereas German and American oils, although likewise soluble in equal volumes of 80 per cent. alcohol, give an opalescent solution, and subsequently a turbid one when more of the solvent is added. The following are the constants noted in Hungarian oils: $d_{15°}$ 0,936 to 0,944, α_D — 38° 38′ to — 46° 25′, $n_{D\,20°}$ 1,490 to 1,491, carvone content 61 to 72%. All the samples gave clear solutions with their own vol. and more of 80 per cent. alcohol; one sample even dissolved clearly in 2,5 vols. and more of 70 per cent. alcohol.

In order to make sure that no carvone from caraway oil had been added to the samples, the carvone was in each case separated out with neutral sodium sulphite and regenerated. The specific gravity was about 0,965 (15°); the rotation lay between — 58° 7′ and — 59° 50′. From the normal character of the rotatory power it is evident that no dextrorotatory carvone from caraway oil was present.

Spike Oil. Under the weight of the commercial depression the prices receded further in the course of the winter, until at last the position induced a few large buyers to cover their requirements. At the present time the stocks in first hand have become greatly reduced, so that the quotations for pure quality have risen from about fr. 5 to fr. 6.50, while in some districts holders are already asking fr. 7. As a result of our holding large stocks, we are for the present able to maintain our prices, but if the upward movement should become more pronounced we shall soon be compelled to follow it.

Birckenstock's[1]) observations with regard to the differences which exist between spike oils derived from plants of different origin have already been discussed by us on a previous occasion[2]).

Spruce Oil. This oil is used in considerable quantities in the United States, principally for liniments and veterinary medicines. It has been distilled in the mountains of Massachusetts, Vermont, and New Hampshire for the past one hundred years or more. This work is done by farmers who have a still in some suitable place on their farms and when other farm work is not pressing, distil oil. This, however, they do only in summer, as none of them put money enough into their outfits so that they could run them in winter.

For distillation the small trees are cut which grow in the pastures and from them the smallest branches are trimmed. The stills consist of wooden tubs and iron worms and generally do not last more than two or three years. Several years ago oil was so low and farm labour so high that the farmers did not renew their stills when they became defective, and failed to work. At that time also some dealers began to buy up spruce brush to be shipped to the cities for use in cemeteries, and $ 4.00 was paid per ton, from which quantity about 15 lbs. of oil can only be obtained.

In 1906 spruce oil was very scarce and prices went up to 65 cts. per lb. Since that time a large number of farmers have put in new stills and oil was run as fast as possible. The farmers offered their oil freely to dealers and wholesale druggists, which caused a heavy decline in price,

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[1]) Journ. de la Parfumerie et Savonnerie **21** (1908), 234.
[2]) Report October **1906**, 73.

the consequence of which will be that no new stills will be put up from now on and that the old stills will not be renewed when out of working order.

Prices may soon advance again. The paper pulp industry is consuming large quantities of trees and as it is reckoned that growing spruce pays ten per cent. interest on its value simply by growing, it can be readily seen why the owners of spruce land hesitate making the trees into oil, unless at a very high figure.

Star anise Oil. Even the price of 4/-, which was reported in November last, did not mark the lowest point touched by the article, for in the month of December a somewhat considerable transaction was actually concluded at 3/11 3/4. Since then, the quotations have moved between 4/- and 4/2, but within the last few days an easier tendency has again manifested itself, and for the present has dashed all hopes of an upward course of the value. Tonquin star anise oil has also been available in plenty last year, but the considerable business which took place was not always concluded without claims, as on several occasions cases filled with stones were found among the consignments. The proceedings which in some instances have been instituted against the shippers of these goods by the insurance companies will, it is hoped, clear up the question whether robbery had been committed during the voyage, or whether irregularities had taken place in the course of shipment at the other side.

Oil of Tagetes patula. In our Report of November **1908**, p. 141, we gave some particulars of the oil of *Tagetes patula L.* obtained from the fresh umbels with the involucre. We are now in a position to add the following details.

We made the umbels (all of which were of the same crop) air-dry, and then subjected them to steam distillation. The yield of oil was 0,08 % from the fresh, and 0,57 % from the dried umbels and was of a brownish yellow colour; it scarcely differed from the oil previously described. Its constants were as follows: $d_{15°}$ 0,8925, α_D — 9°, $n_{D20°}$ 1,49938, acid no. 6,4, ester no. 10,6, soluble in 9 to 10 vols. of 90 per cent. alcohol, producing cloudiness; miscible with 95 per cent. alcohol.

The oil obtained from the air-dried stalks and leaves by water-and-steam-distillation showed similar properties. Of this oil we obtained 0,07 % from the fresh, and 0,218 % from the dried herb. $d_{15°}$ 0,9034; α_D + 1° 15′; $n_{D20°}$ 1,49938; acid no. 14; ester no. 12,4 (after heating again the ester no. was 10,6); not clearly soluble in 10 vols. of 90 per cent. alcohol; miscible with 95 per cent. alcohol. From the saponification-liquors, a fatty acid (palmitic acid) m. p. 62°, could be separated after repeated re-crystallisation.

Tansy Oil. Good American oil continues to remain very scarce, and the small supplies which we have obtained through the intermediary of our New York branch, have quickly found buyers at full prices.

Tetranthera Oils. The Buitenzorg Annual Report for 1907[1]), contains brief references to tetranthera oils which, like those examined by Charabot and Laloue and mentioned in our Report of April last[2]), were produced in the Malay Archipelago, in the Island of Java. The Buitenzorg examinations related to three distillates, one each from the bark, the leaves and the fruit respectively, and resulted as follows: —

1. Oil from bark. Yield about 0,13 %, $d_{26°}$ 0,856, α_D + 20° 24′, contained 78,5 % aldehydes.

2. Oil from leaves. $d_{26°}$ 0,890, α_D — 12° 12′, contained much cineol and 22 % aldehydes.

3. Oil from fruits. Yield about 3,9 %, $d_{26°}$ 0,876, α_D + 12° 44′, on fractional distillation, 19 % passed over up to 200°, 61 % between 200 and 220°, and 14 % between 220 and 240°. The oil contained 85 % aldehydes, of which 64 % was citral.

In connection with the above we may here refer to our own results, obtained with tetranthera oils from the same source: —

An oil from bark possessed the following characteristics: $d_{15°}$ 0,9062, α_D + 13° 58′, $n_{D20°}$ 1,46595, ester no. after acetylation 230,2, soluble in 1 vol. and more of 80 per cent. alcohol. This oil was of a pale-yellow colour; its odour reminded of Java citronella oil, and it obviously contained much citronellal, 76,5 %, judging from the acetylation number.

An oil from leaves was also pale-yellow and had a pronounced cineol-odour. It contained, in fact, about 35 % of this body, obtained with resorcinol in the form of a solid compound. Other components parts were citral (6 % determined with neutral sulphite) and probably also citronellal. The constants were as follows: $d_{15°}$ 0,8990, α_D — 12° 2′, $n_{D20°}$ 1,46426, soluble in 1 vol. and more of 80 per cent. alcohol. The diluted solution opalesces.

Two oils distilled from fruits were of a lemon-yellow colour and possessed an odour somewhat like that of lemongrass oil, which is accounted for by the fact that their principal constituent was citral. As the aldehyde determinations with bisulphite gave higher figures than did those with neutral sulphite, it follows that in addition to citral other aldehydes (citronellal, fatty aldehydes) which do not react with neutral sulphite, must be present.

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[1]) Jaarboek van het Departement van Landbouw in Nederlandsch-Indië **1907**, 67. Batavia 1908.

[2]) Report April **1908**, 100.

a) $d_{15°}$ 0,8932, α_D + 6° 8′, $n_{D20°}$ 1,48141, soluble in 2,3 vol. and more of 70 per cent. alcohol, aldehyde content determined with bisulphite about 85 %, with neutral sulphite about 75 %.

b) $d_{15°}$ 0,8849, α_D + 11° 30′, soluble in 3 vol. and more of 70 per cent. alcohol, from 5 vol. and upwards increasing opalescence. Aldehyde content 79 % (bisulphite) or 74 % (neutral sulphite).

Oil from Thuja plicata (Red Cedar). In our recent Reports[1]) we have dealt with the investigations made by Blasdale and by Brandel and Dewey respectively on the oil prepared from the leaves of *Thuja plicata* (red cedar), a native of North America. We have recently distilled a similar oil ourselves from the air-dried leaves of trees which had been planted in the South of France, Prof. Heckel, of Marseilles, having very kindly procured for us the material for distillation. The oil, which was obtained to the extent of 1,32 %, was of a pale yellow colour and possessed a strong odour of thujone: $d_{15°}$ 0,9056, α_D + 5° 4′, $n_{D20°}$ 1,45721, acid no. 0,8, ester no. 16,9, soluble in 70 per cent. alcohol with opalescence only (about 1:8) but giving a clear solution in 1,2 vols. and more of 80 per cent. alcohol. The thujone separated from the oil with the aid of semicarbazide proved to be identical with α-thujone; the semicarbazone melted at 185 to 186° after being twice re-crystallised from alcohol, and the thujone regenerated from it with phthalic anhydride had a rotation of α_D — 5° 12′.

We desire to call special attention to the fact that Blasdale's oil and our's were dextrorotatory, while Brandel and Dewey describe their oil to be lævorotatory.

The botanical names in use for the American tree may also be of interest, and are therefore set forth below: *Thuja plicata* Lamb. non Don., *Th. gigantea* Nutt., *Th. Menziesii* Dougl., *Th. Douglasii* Nutt. and *Th. Lobii* hort. (or rather *Th. Lobbi* hort.; the name being derived from Lobb, who introduced the tree into Europe from Western North America in 1853).

Turpentine Oil. An announcement on the part of the Government of Algeria[2]), to the effect that the Forestry Authorities intend, in the course of the month of March, to sell by auction ten *"Coupes de regéneration"* covered with Aleppo pines and occupying a total area of about 550 hectares, situated in the districts of Télagh and Bel-Abbès, appears to show that the manufacture of turpentine distillates is receiving attention in other regions than those in which the production of turpentine oil is being carried on at present. In the case of six of these timber-felling plots it will be allowed to tap the trees

[1]) Report October **1907**, 91; November **1908**, 117.
[2]) Bull. de l'Office du Gouvern. Gén. de l'Algérie **15** (1909), 50.

four years in succession until they are exhausted (*"à mort"*) and to cut them down to the stump in the fifth. It is estimated that these plots will yield about 6500 cubic metres of timber and about 400 hectolitres of resin. The trees in the other four plots, estimated at about 30000, may only be tapped for four years without killing (*"à vie"*). A small plan of the site which accompanies the announcement shows the position of the separate plots and the distance of each from the main lines of traffic.

According to R. Adan[1]), when examining oil of turpentine for the presence of mineral oil, the old Burton's test is to be preferred to Herzfeld's process[2]), because the formation of a residue insoluble even in fuming sulphuric acid does not suffice to prove the presence of benzine, inasmuch as the said residue may also owe its existence to the presence of resin spirits. The best way of carrying out Burton's test is by pouring, drop by drop, 100 cc. of the oil into 300 cc. of fuming nitric acid, and by weighing or measuring the insoluble residue (which should not exceed 2 %), after washing it out with hot water. Pure resin spirits ($d_{15°}$ 0,8656, $n_{D15°}$ 1,4826), when treated with nitric acid, yielded only 2,1 % of residue ($n_{D15°}$ 1,455); but when treated with sulphuric acid they yielded as much as 17 % ($d_{15°}$ 0,8472, $n_{D15°}$ 1,463). Fractional distillation of the resin spirits resulted as follows: 8 % of a b.p. from 118 to 150°, 51 % of b.p. 150 to 180°, 27 % of b. p. from 180 to 220°, 10 % of b. p. 220 to 295°; residue 4 %. Burton's test is therefore also well suitable for detecting the presence of benzine in resin spirits. If, in addition, the parts which boil over between 120 and 150° are miscible with aniline and acetic anhydride, the absence of benzine is established.

Wintergreen Oil. Owing to a plentiful output and a somewhat diminished sale, the prices have slowly receded, and a sufficiency of oil of sweet birch of reliable quality is available. The production has again increased, both in Pennsylvania and in the more Southern States. The present low price should be an inducement to lay in a sufficient supply, as it is known that during the summer the producers are otherwise occupied, while the increasing consumption tends to put up the prices.

Oil of Wintergreen leaves. The demand for genuine oil of Gaultheria existing exclusively in the United States has been rather less than in the preceding year and we have therefore been able to supply all the requirements of our customers.

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[1]) Bull. Soc. Chim. Belgique **22** (1908), 389. Quoted from Chem. Zentralbl. **1908**, II. 1749.

[2]) Report April **1904**, 85 and 86.

As we have repeatedly stated, our New York branch disposes of the output of several suppliers of established repute, whose names we are of course precluded from publishing on account of business considerations.

Although the majority of our suppliers are personally known to us, every delivery which reaches us is subjected to the most severe chemical examination, and we are in a position fully to differentiate between synthetic oil, sweet birch oil, and oil of wintergreen leaves. Quite recently, parties in Carolina and in New England have taken up the distillation of *Gaultheria procumbens*, and we are expecting sample-consignments of this oil.

H. D. Gibbs[1]) reports on the separation of salicylic acid and methyl salicylate, as well as on saponification-experiments made with the ester, problems occurring in the examination of pharmaceutical preparations or of lemonades and other non-alcoholic beverages. The two compounds above mentioned often occur together and it is possible (apart from deliberate addition) that the presence of the acid or its salts may be due to the existence, as an impurity, of free acid in the synthetic ester, wintergreen oil, or sweet birch oil which has been used, or that a splitting-up has occurred. The free acid can be titrated directly. In order to separate it from the ester it is first extracted by frequent shaking with a solution of bicarbonate of sodium of known strength; from this, the ester is removed with chloroform, after which it is acidulated with sulphuric acid 1 : 3, shaken out with chloroform and determined by titration or by the colorimetric process. By this method, samples of synthetic ester were found to contain 0,0113 %, such of wintergreen oil 0,025 to 0,028 % of free acid. In the examination of cod liver oil emulsions the bicarbonate-layer was removed by centrifugal action. The ester extracted by chloroform was saponified by boiling it for half an hour with solution of caustic alkali, after which the chloroform was driven off, the sample under examination filled up to a known volume in an aliquot part of the solution and the salicylic acid content determined. Experiments on the rate of saponification of the ester by means of carbonate and bicarbonate of sodium (by shaking solutions of known strength with an excess of of ester at 30°), showed that when sodium carbonate was used equilibrium was reached in about a month's time, when the whole of the carbonate had been converted into bicarbonate, whereas in the case of bicarbonate no perceptible saponification was to be observed. When caustic soda solution was employed the saponification was completed in about 24 hours.

[1]) Journ. Americ. chem. Soc. **30** (1908), 1465. Philippine Journ. of Science **3** (1908), A. 101.

Furthermore, Gibbs[1]) determined the solubility of methyl salicylate in water and in $^1/_{10}$ normal sulphuric acid at 30° C. The former solubility was found to be on the average 0,074 g, the latter 0,077 g, each for 100 cc. solvent.

We can only briefly mention here an article by G. R. Pancoast and W. A. Pearson[2]) on methods for distinguishing between natural and artificial methyl salicylate. We abstain from a detailed description of the process, because the methods indicated are hardly likely to effect their object in a manner which is at all desirable for practical purposes.

Wormwood Oil. The scarcity of French oil, which has arisen from causes which we have already explained, has become more and more pronounced, and as our supplies grew less we were compelled to raise the prices in proportion. It will probably be necessary shortly to look forward to the entire disappearance of this article from commerce. American oil also remains very scarce and dear, and has again advanced in price, which is not surprising, seeing that the demand for this variety has naturally become greater lately.

To the statements made in our Report April **1908**, 119, on the projected prohibition of absinthe throughout the Swiss Confederacy, we are now able to add the information that as the result of the *Referendum* of 5th July 1908, the Swiss People have passed a resolution prohibiting, as from October 7th 1908, the manufacture, importation, transport, sale, and storage for the purposes of sale, throughout Switzerland, of the liqueur known as "absinthe".

The prohibition also applies to all beverages, by whatever other name they may be called, which are imitations of this liqueur. Only the transit trade and the use for medicinal purposes are still permitted. The Act comes into force two years after the date of its passing, that is to say, on October 7th, 1910. The executive of the Confederacy is empowered to issue similar prohibitions in respect of all other beverages containing absinthe which constitute a public danger.[3])

L. Duparc and A. Monnier[4]) have modified Legal's test (recommended by Rocques[5]) for the determination of thujone in liqueurs, and they claim that their method obviates a confusion of thujone with other compounds, including citral. The process is as follows:

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[1]) Philippine Journ. of Sc. **3** (1908), A. 357.
[2]) Americ. Journ. Pharm. **80** (1908), 407.
[3]) Chemische Industrie **32** (1909), 134.
[4]) Ann. chim. analyt. appl. **13** (1908), 378. Quoted from a copy kindly sent to us.
[5]) Comp. Report November **1908**, 127.

10 cc. of a solution in 60 % alcohol of the sample under examination are first treated with 2 cc. zinc sulphate solution (1 : 10) and afterwards with 0,5 cc. of a solution of sodium nitro-prusside (1 : 10). After shaking, 4 cc. of 5 % sodium solution, free from carbonic acid, are added, and one minute later 2 to 3 cc. of glacial acetic acid. The currant-coloured precipitate formed is claimed to indicate the presence of thujone even in dilutions up to 1 : 5000. It settles in the course of a few minutes. If a garnet-red coloration should ensue upon the addition of the acetic acid it can be removed by shaking with ether. In the case of all other bodies which have been investigated, citral excepted, the precipitate is of a paler colour. Any citral which may be present should therefore be removed in advance by prolonged boiling with aniline phosphate.

In connection with the above reference may be made to a work by L. Duparc on liqueurs seized, designated as imitations of absinthe. This work, which has been published as a pamphlet[1]), deals with the manufacture of absinthe, the composition and especially the toxic character of the essential oils used, and their emulsifying properly. It also contains detailed references as to the definition of absinthe and the various methods employed for its analysis.

Ylang Ylang Oil. The sale of this oil, which is so important an article in the perfume industry, has suffered severely during the past half year from the general depression, although the suddenly acquired popularity of Lily-of-the-valley scents opened up a new and favourable prospect, especially for our recognised first-class quality Even in spite of the excellent artificial Lily-of-the-valley scents which are now available, the use of ylang ylang oil cannot be dispensed with in the preparation of high-class perfumery of this kind.

In our last report we referred briefly to the exports of ylang ylang oil from Réunion. Complete statistics are now available as to the shipments of this oil from the island for the whole of the year 1908. These show that in the period named 1126 kilos were exported, compared with 523 kilos in 1907. The production has therefore more than doubled. The samples of Réunion oil which we have had an opportunity of examining, although showing normal characteristics, cannot compare in odour with first-class Manila quality.

According to a report issued by the Bureau of Insular Affairs[2]) the sale of ylang ylang oil in the Philippines in the fiscal year 1908 reached the exceptionally high value of $ 181638.

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[1]) L. Duparc, Rapport d'expertise sur les liqueurs saisies qualifiées d'imitations de l'absinthe. Geneva, **1908**.

[2]) Nachrichten für Handel und Industrie **1909**, Nr. 4, p. 2.

Roure-Bertrand Fils[1]) have ascertained the following values in an ylang ylang oil from Réunion. The figures agree with those of Manila oil: $d_{15°}$ 0,9492, α_D — 30° 8′. Ester content (calculated as linalyl acetate) 33,6 %, total alcohol (calculated as linalool) 40,3 %. Soluble in 0,5 to 1 vol. of 90 % alcohol, followed shortly afterwards by slight cloudiness.

A Réunion oil examined by us years ago[2]) showed the high specific gravity of 0,974 (15°).

In an article by M. Mücke[3]) on the plant yielding ylang ylang oil, and the production of the latter, we find *inter alia* a few details concerning cultivation experiments at Amani which have been carried out by the German Biologico-Agricultural Institute. According to these experiments, the ylang ylang tree appears in the said district not to thrive very well at altitudes of 900 m.; but it does well at up to 450 m. altitude. Mücke assumes that the limit of altitude of the ylang ylang tree lies between 500 and 550 m. This assumption appears to correspond with the statement by Flacourt[4]) relating to Réunion, which has a more southerly position and where the limit of altitude of the tree is about 400 m.

New essential oils.

Oil from Barosma pulchellum. In addition to the varieties of Barosma which are of interest in the preparation of buchu leaf oil, i. e. *Barosma betulinum* (Thunb.) Bartl. et Wendl., *B. crenulatum* (L.) Hook., and *B. serratifolium* (Curt.) Willd., the leaves of other species have lately been met with in the London market on several occasions. Some years ago, Sage[5]) reported on leaves of *Diosma succulentum* var. *Bergianum*, known as Karoo Buchu, which are reputed to yield an oil equalling that of *Barosma betulinum* in value. In other quarters, however, leaves have also been noticed of which the oil, by its mere odour, betrays a composition differing materially from that of the ordinary buchu leaf oil. The leaves of *Barosma pulchellum* (L.) Bartl. et Wendl., as well as those probably derived from *Agathosma variabile* (Lond.) belong to the latter category. The last-named leaves have also been described by Sage[6]) who, on account of their anise-like

[1]) Berichte of Roure-Bertand Fils, October **1908**, 29.
[2]) Gildemeister and Hoffmann, *The Volatile Oils*, p. 364.
[3]) Der Pflanzer **4** (1908) 257.
[4]) Comp. Report April **1904**, 89.
[5]) Chemist and Druggist **65** (1904), 506, 717. Report April **1905**, 12.
[6]) Pharmaceutical Journal **80** (1908), 125.

odour, called them "Aniseed Buchu". These leaves are ovate-lanceolate, leathery, 5 to 8 mm. long and 3 mm. wide and bear a resemblance to Karoo Buchu. Sage intends to make further investigations with the object of discovering whether the botanical designation aforementioned is correct.

E. M. Holmes[1]) was the first to call attention to the occurrence of leaves from *Barosma pulchellum*. They differ from the *betulinum* leaves by their citronella-like odour as well as by being smaller. Their length runs from 7 to 12 mm., their width is 4 mm. They have very short stalks, are ovate to ovate-lanceolate, serrulate, obtuse, and broadest at the base of the leaf. Like the other varieties of *Barosma*, the shrub is a native of Cape Colony. In order to enquire further into the question whether the oil would eventually possess a commercial value, we obtained from London a considerable parcel of the leaves. Dr. Giessler, "Custos" at the Botanical Institute of Leipzig University, who has examined the material as regards its botanical origin, has ascertained that it really represented *Barosma pulchellum* (L.) Bartl. et Wendl. Leaves of the closely related *B. pulchellum* var. *majus* and *B. latifolium* (L. f.) Röm. et Schult. also occurred in the parcel.

Upon distillation the leaves yielded 3 % of a golden-yellow oil, with an odour reminding chiefly of citronella, but possessing at the same time an unpleasant narcotic subsidiary odour, which constitutes a direct objection to the use of the oil. The specific gravity was 0,8830 (15°), opt. rot. α_D +8° 36′, $n_{D20°}$ 1,45771, acid no. 18,5, ester no. 27,2, ester no. after acetylation 237,0 = 79,3 % $C_{10}H_{18}O$. We are able to give the following details with regard to the examination of the oil, which is however not yet concluded: —

The disagreeable subsidiary odour referred to above is due to a base. This was abstracted from the oil (which was kept cool) by treatment with 25 % tartaric acid solution. The base, separated from the tartaric acid solution by means of carbonate of soda, possessed an extraordinarily penetrating narcotic odour. It had a rather inconstant b. p. between 130 and 140° (5 mm. press.). (The quantity of the material employed was barely 1 g.) From the hydrochloric acid solution, on treatment with platinum chloride, no crystals separated off.

The citronella-like odour of the oil freed from the base made us suspect the presence of citronellal. As a matter of fact the oil reacted with bisulphite liquor partly neutralised by sodium carbonate, a crystalline mass being separated. From the latter, after filtering with the suction pump and purifying with alcohol and ether, an aldehyde was liberated by warming with carbonate of soda solution. Its constants showed it to be citronellal;

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[1]) Pharmaceutical Journal **79** (1907), 598; compare also Chemist and Druggist **71** (1907), 702.

b. p. 73 to 75° (7 to 8 mm. press.), b. p. 205 to 208° (atmosph. press.), $d_{15°}$ 0,8560, α_D + 13°6′, $n_{D20°}$ 1,44710. Its semicarbazone melted at 81 to 82°. From 500 g. of oil we isolated about 220 g. of aldehyde. The smaller part of the oil freed from citronellal passed over between 45 and 103° (5 mm. press.), the larger portion remained behind in the flask in the form of a brown, viscous oil. The fractions with the lowest b. p. contained small quantities of methylheptenone, which was separated in the form of a semicarbazone. Only after recrystallising it three or four times from dilute alcohol the m. p. of this derivative was found to be 134 to 135°. This circumstance, as well as the fact that when the odour observed was not that characteristic of methylheptenone, but rather reminded of a saturated fatty ketone, indicated the presence of another, additional, ketone. The semicarbazone referred to above, when mixed with that from the pure methylheptenone, showed no depression of the melting point.

In a fraction having the b. p. 75 to 82° (5 mm. press.) and the opt. rot. + 6° 54′, small quantities of d-menthone could be detected, but only through the semicarbazone. Only when the oil mixed with it had been removed from the semicarbazone solution by steam distillation, the derivative could be obtained in the solid form. After repeated recrystallisation from alcohol it melted at 178 to 181° and when warmed with diluted acid it developed the unmistakable odour of menthone. Efforts were also made, unfortunately without success, to separate by means of the oxime larger quantities of menthone from the fractions which preceded and succeeded the one referred to above, and to reconstitute the ketone from them. It is therefore probable that the somewhat pronounced odour of mint which attached to all these fractions is ascribable to the presence of isopulegol. This isopulegol obviously owed its existence to the action of acids upon the citronellal.

Further, in the portions of the oil boiling between 75 and 103° (5 mm. press.) we discovered an alcohol of a rose-like odour, which was ascertained to be d-citronellol. For the purpose of identification the fractions were treated in the well-known manner with phthalic anhydride. The citronellol separated by saponification from the solution of the sodium salt of the acid phthalic ester and distilled over with water vapour, possessed the following constants: b. p. 93 to 95° (5 to 6 mm. press.), $d_{15°}$ 0,8732, α_D + 2° 14′, $n_{D20°}$ 1,46288. The silver salt prepared from the free acid phthalate, after being recrystallised from benzene and methyl alcohol, showed the characteristic melting point for this salt (125°) and the theoretically required silver content: —

0,2774 g. sbst.: 0,0727 g. Ag.

Found:	Calc. for $C_{18}H_{21}AgO_4$:
Ag 26,21 %	26,23 %

When the original oil was treated with highly-diluted soda liquor it proved to contain an oily acid of a high b. p. as well as traces of a phenol. In order to separate these two the oil, after being recovered from the soda liquor, was treated with carbonate of soda solution. The acid which had separated from the carbonate solution on acidulation may, however, not be a uniform one, as might be concluded from its b. p. and its behaviour as detailed below. Apart from an unimportant first runnings (b. p. 115 to 125°, 5—6 mm. press.) it boiled at 125 to 131°. Its other constants were as follows: b. p. 257 to 263° at normal press., $d_{15°}$ 0,9394, α_D + 5° 2′, $n_{D20°}$ 1,45611. These properties, and the silver content as ascertained by analysis of its silver salt recrystallised from water, indicate citronellic acid $C_{10}H_{18}O_2$: —

0,3079 sbst.: 0,1196 g. Ag.

Found:	Calc. for $C_{10}H_{17}AgO_2$:
Ag 38,84 %	38,77 %

In order to identify the acid more closely recourse was had to the amide of citronellic acid, m. p. 81 to 82°. For its preparation, the acid was first converted into the chloride (b. p. 122 to 125°, 6 mm.) by means of thionyl chloride, and the latter converted into the amide with aqueous ammonia. The amide purified from petroleum ether melted not quite sharply at 87 to 88°, that is to say, 6° higher than that obtained by Tiemann[1]) from citronellic acid nitrile. It is our intention, for purposes of comparison, to prepare the amide of synthetic citronellic acid, in order to determine by this means whether the above-mentioned acid really represents citronellic acid (the existence of which in essential oils has not been detected up to the present), or another acid of the same constitution. In addition to the arguments adduced above, its identity with citronellic acid seems to be indicated by the fact that the oil contains both citronellol and citronellal.

Only traces of the phenol referred to above were at our disposal. These were just sufficient to enable us to identify it by its benzoyl combination. This body, obtained by Schotten-Baumann's method, when purified from petroleum ether, had a m. p. of 109 to 110°, but up to the present we have been unable to identify it with the benzoate of any known phenol.

From the Instituto Médico Nacional in Mexico we received the two following distillates: —

Oil of Satureja macrostema (Benth.) Briq. (*Calamintha macrostema* Benth.). The oil of this shrub-like plant, which belongs to

[1]) Berl. Berichte **31** (1898), 2899.

the N. O. *Labiatæ* and is a native of Mexico, was pale yellow and had an odour resembling that of mint; $d_{15°}$ 0,9182, α_D + 6° 51′, $n_{D20°}$ 1,46852, acid no. 15,6, ester no. 10,3, ester no. after acetylation 37,9. The oil is soluble in any proportion of 90 per cent. alcohol, also in 3 vols. of 70 per cent. or 1,2 vol. of 80 per cent. alcohol, but opalescence ensues with the last two when more of the solvent is added. The odour points to the presence of pulegone.

Oil from the Mexican Marsh-cypress (*Taxodium mexicanum* Carr., *T. Montezumae* Decne., *T. mucronatum* Ten.). This tree, which belongs to the conifers and is known in Mexico as "Sabino", grows in that country at altitudes of from 5600 to 7000 ft. It is not distributed over a very wide area, but where it does grow it forms large forests.[1]) The oil, which had probably been distilled from the leaves, was of a pale brown colour and somewhat resembled, in its odour, oil of turpentine, to which it is probably also closely allied in its composition. $d_{15°}$ 0,8685, α_D — 10° 20′, $n_{D20°}$ 1,46931, acid no. 0,5, ester no. 5,7; soluble in 5,4 vols. and more of 90 per cent. alcohol.

Oil of Artemisia Herba-alba var. densiflora Bois (Chieh Oil). From Egypt we received, for the purpose of examining it for essential oil, a herb which is known there by the name of "Chieh", and which occurs on the high limestone plateaus of Egypt and Tripoli and probably also in Arabia. The plant is said to reach its full development early in March and to flourish particularly in rainy years. The Arabs and Tuaregs employ a decoction of the herb medicinally as an emollient and diuretic. Owing to the sample sent to us being imperfect, great difficulty was experienced in determining its botanical name. Prof. Heckel, of Marseilles, who kindly examined the sample for us, and to whom we owe thanks for his courteous assistance, informed us under reserve that the herb was probably an *Artemisia Herba-alba*. This opinion was confirmed on further investigation when a few specimens which had been carefully pressed between paper were sent to us. Dr. Giessler, "Custos" at the Botanical Institute of the University of Leipzig, was able to ascertain that the sample represented a variety of the above-mentioned plant, viz., *A. Herba-alba* var. *densiflora* Bois.

By water vapour we obtained from it a yield of 1,6% of a yellowish oil, with a clear odour of thujone, which upon examination gave the following results: $d_{15°}$ 0,9192, α_D — 5° 20′, $n_{D20°}$ 1,45611, acid. no. 1,5, ester no. 11,0, ester no. after acetylation 40,7, soluble

[1]) The famous "Cypress of Montezuma" in the cemetery of Santa Maria del Tule near Oaxaca belongs to the same variety. It is said to be 130 ft. high, the trunk to have a circumference of 98 ft. De Candolle estimated its age at 6000 years, Humboldt at 4000.

in 2,6 vol. and more of 70 per cent. alcohol. From the low ester and acetylation numbers it is to be inferred that the oil contains but small proportions of saponifiable and alcoholic constituents.

With regard to an oil of *Artemisia Herba-alba* previously examined by E. Grimal, compare our Report October **1904**, 13. This oil differs entirely from the one now under review, which may without further enquiry be set down to the fact that *A. Herba-alba* shows very wide variations. Several varieties exist which have been regarded as separate species by many authors; J. Gay, for instance, describes the variety above-mentioned as *A. Oliveriana.*

Pharmacopœias.

The British Pharmaceutical Codex 1907.

In our previous April Report[1]) we expressed ourselves in detail on the subject of the requirements fixed in the British Pharmaceutical Codex, published in the year 1907, for essential oils and their constituents. A similar review has now been published by C. T. Bennett[1]) in the *Pharmaceutical Journal.* Without entering into further details we will content ourselves with the observation that our opinions differ from those of Bennett on many points, and that we maintain our former criticism in every particular. We recommend that in judging oils our observations should be taken as the basis, as otherwise erroneous conclusions might perhaps be arrived at concerning this or that oil.

Swedish Pharmacopœia.

(Pharmacopœa suecica, ed. IX.)

On January 1st a new edition (the ninth) of the Pharmocopœia came into force in Sweden. Unfortunately we were unable to discuss it in our last Report, before the actual date when came into force because although we ordered a copy of the book in good time, it only reached us in November 1908. So far as concerns the articles in which we are specially interested, we may repeat what we wrote when discussing the eighth edition[2]), namely that in their statements as to properties and tests the editors have everywhere been careful to take account of the actual state of science. But we wish to lay special stress upon the fact that the criticisms which we then offered have throughout been taken into consideration in the new Pharmacopœia, so that there is little left for us to say concerning the

[1]) Report April **1908**, 134.
[2]) Report April **1902**, 68.

present edition. Unfortunately it is true that one important alteration, that with regard to the determination of the boiling points, has not been carried out. At the time we pointed out specially that, in order to obtain accurate results, the whole of the mercury column concerned must be surrounded by the steam of the liquid. The barometric pressure must also be considered. But in the "allmänna föreskrifter" (general rules) nothing is said as to this; on the contrary, the prescriptions relating to the determination of the boiling point have been reprinted without alteration from the eighth edition; which lays it down that the thermometer should be so arranged that the mercury bulb is placed immediately below the lateral delivery tube. Under such conditions there can be no doubt that in many boiling point determinations only a portion of the mercury column will be exposed to the steam from the liquid and that the thermometer, in such cases, will be quite unable to register the actual boiling point, so that the results will require correction. In order to obtain accurate values the thermometer must be fixed in such a manner that the degree of the boiling point is slightly above the delivery tube, but care should be taken that the mercury bulb does not protrude into the bulb of the flask, or even into the liquid itself. Shortened thermometers are the best adapted for tests of this kind. It is almost impossible to lay too much stress upon the importance of this condition, for in most cases where objections are raised it is found that claims based on an alleged improper boiling point have their ground in a defective testing method.

No oil has been newly introduced into the Pharmacopœia, while oils of fennel and mace are no longer official.

The enumeration of the separate essential oils is prefaced by a short general chapter on properties and method of keeping, as well as on tests for alcohol and fatty oil.

Among the alcohols, a change has been made in *Spiritus dilutus*, its alcoholic strength having been raised, the following being the strengths now prescribed:

Spiritus concentratus (Sprit): 90,3 to 91 %,
„ *dilutus* (Utspädd sprit): 69,6 to 70,5 %,
„ *tenuis* (Svag sprit): 48,4 to 50,6 %.

By "parts" the Pharmacopœia understands "parts by weight".

Anethol (*Anetholum*). The solid constituent of oil of anise[1]). A white, leaf-like, crystalline mass, which melts into a colourless or faintly yellow[2]), somewhat thickish liquid; $d_{25°}$ 0,984 to 0,986, $\alpha_D \pm 0°$, congeals at about 20°[3]) and melts at 21 to 22,7°, b. p. 233 to 234°, gives a clear, neutral solution with less than 2 parts of *spiritus conc.* at 20°[4]).

Anethol is to be dispensed in lieu of anise oil and of fennel oil.

[1]) Anethol from star anise oil or fennel oil is completely identical with that from anise oil.

[2]) Good anethol is always colourless.

[3]) The congealing-point of a good preparation lies between 21 and 22°; when the oil is imperfectly kept it falls considerably. Compare Report October **1904**, 42.

[4]) In order to dissolve 1 vol. anethol, 2 to 3 vol. 90 per cent. alcohol are required.

Camphor (*Camphora*). A white, fatty, lustrous, tough, crystalline mass, m. p. 175 to 177°, b. p. 204 to 208°; burns with a highly luminous flame; sparingly soluble in water, readily soluble in alcohol, ether, chloroform, fatty and essential oils. Camphor should be completely soluble in *spiritus conc.* and, when slightly warmed, should sublime without leaving a residue.

Carvone (*Carvonum*). Colourless or faintly yellow; $d_{15°}$ 0,963 to 0,966; α_D to the right[1]); b. p. 229 to 230°; soluble in any proportion in *spiritus conc.* and at 20° in 20 parts *spiritus tenuis*; test with ferric chloride. Carvone is to be dispensed in lieu of caraway oil.

[1]) The rotation lies between + 57 and + 60°.

Cinnamic aldehyde (*Cinnamalum*). Yellowish; $d_{15°}$ 1,054 to 1,056[1]); $\alpha_D \pm 0°$; congeals when strongly cooled and melts again at — 7,5°; b. p. about 252° under partial decomposition; soluble in any proportion in *spiritus conc.;* nitric acid test; silver mirror; ferric chloride reaction; test for chlorides. Cinnamic aldehyde when heated with a solution of bisulphite of sodium should dissolve completely. Cinnamic aldehyde is to be dispensed in lieu of cassia oil.

[1]) In our own preparations, we have observed up to 1,058.

Eucalyptol (*Eucalyptolum*). Colourless or faintly yellow[1]) $d_{15°}$ 0,928 to 0,930; $\alpha_D \pm 0°$; b. p. 176 to 177°; when strongly cooled down, it congeals to a white, crystalline mass which melts at — 1°[2]); soluble in any proportion in *spiritus conc.*; reaction with bromine. Eucalyptol is to be dispensed in lieu of cajeput oil and eucalyptus oil.

[1]) A good article is always colourless.

[2]) The m. p. lies between + 1 and + 1,5°. Compare Report October **1907**, 49. Congelation should, if necessary, be induced by rubbing the side of the vessel with a glass rod.

Eugenol (*Eugenolum*). Bright yellow; darkens in course of time; $d_{15°}$ 1,070 to 1,074; $\alpha_D \pm 0°$; b. p. 251 to 253°; soluble in any proportion in *spiritus conc.* and in ether, also in 2 vol. *spir. dil.* With an equal volume of caustic soda solution (25% NaOH) eugenol should yield a solid crystalline mass. Ferric chloride reaction.

Lavender Oil (*Aetheroleum Lavandulae*). Bright yellow or bright greenish yellow; $d_{15°}$ 0,885 to 0,895; α_D slightly to the left[1]). Sap. no. not below 90[2]); soluble in any proportion of *spiritus conc.*

[1]) The rotation lies between — 3 and — 9°.

[2]) Corresponds to a minimum content of 31,5% linalyl acetate.

Lemon Oil (*Aetheroleum Citri*). Bright yellow; $d_{15°}$ 0,855 to 0,861[1]); $\alpha_{D\,20°}$ + 58 to + 65°; usually not quite clearly soluble in 5 parts of *spiritus conc.* Oil of lemon should only have a slight deposit and give no strongly acid reaction.

[1]) Pure oils of less than 0,857 sp. gr. are very rare, and we have only on very exceptional occasions observed a sp. gr. so low as 0,856, never one below that figure.

Menthol (*Mentholum*). Colourless, brittle crystalline needles, almost insoluble in water, readily soluble in *spiritus conc.*, ether, chloroform and fatty oils; m. p. 43°[1]); b. p. 212°[2]); 0,1 g. menthol, when heated on the water-bath, should evaporate without leaving a residue.

[1]) The m. p. lies between 43,5 and 44,5°.

[2]) Menthol boils at 217° when the mercury column of the thermometer is wholly surrounded by the vapours. See Introduction.

Mustard Oil (*Aetheroleum Sinapis*). Colourless or pale yellow; $d_{15°}$ 1,016 to 1,025[1]); $\alpha_D \pm 0°$; soluble in any proportion in *spiritus conc.*, ether, benzene and carbon disulphide. On distillation the bulk should pass over between 147 and 152°, and the sp. gr. of the first, as well of the last, fraction should not differ materially from that of the original oil; thiosinamine and sulphuric acid tests; ferric chloride reaction; isothiocyanallyl content 82,3 to 100%[2]).

[1]) We have found pure oils to have as low a sp. gr. as 1,014.

[2]) The present edition of the Pharmacopœia prescribes a test which differs from the older method to this extent that the mustard oil is no longer to be left standing with the ammoniacal silver solution for 24 hours at normal temperature, but only for 1 hour at a temperature of about 75°. See our Report April **1908**, 70.

Peppermint Oil (*Aetheroleum Menthae piperitae*)[1]). Colourless, yellowish or faintly yellow green; $d_{15°}$ 0,90 to 0,92; α_D to the left; 1 part of oil should give a clear, or at most a faintly opalescent solution with 3 to 4 parts of *spiritus dil.* Iodine reaction[2]).

[1]) English as well as American oil answers these requirements.

[2]) Reactions of this kind are out of date and purposeless.

Rosemary Oil (*Aetheroleum Rosmarini*). Colourless or bright greenish yellow; $d_{15°}$ 0,90 to 0,92; α_D to the right; soluble in 0,5 parts of *spiritus conc.*

Sandal Oil (*Aetheroleum Santali*). Bright yellow, somewhat viscid; faintly acid reaction; $d_{15°}$ 0,975 to 0,985; $\alpha_{D\,20°}$ — 17 to — 20°[1]) soluble in any proportion in *spiritus conc.* and in from 5 to 6 parts of dilute alcohol.

[1]) As we have been able to observe in our own, normal distillates, the rotation is occasionally a little less. Compare Report October **1905**, 64.

Thymol (*Thymolum*). Colourless, transparent crystals, soluble in water (1100 parts), glycerin (100 parts) and very readily in *spiritus conc.*, ether and chloroform, also soluble in fatty and essential oils and in soda solution; m. p. 50 to 52°, b. p. 228 to 230°[1]). When solid thymol sinks in water; in tho molten state it floats upon it; 0,2 g. of

thymol should evaporate on the water bath without leaving a residue; identity-reaction; test for phenol.

[1]) Thymol boils between 233 and 234° when the mercury column is entirely surrounded by the vapours. Compare Introduction.

Turpentine Oil, crude (*Aetheroleum Terebinthinæ crudum*). Colourless or faint yellow; $d_{15°}$ 0,860 to 0,875; b. p. 150 to 162°; should have no empyreatuatic smell.

Turpentine Oil, purified (*Aetheroleum Terebinthinæ depuratum*). Colourless; $d_{15°}$ 0,860 to 0,870; b. p. 155 to 162°; soluble in 10 to 12 parts of *spiritus conc.*; 5 g. of oil when allowed to evaporate on the water bath must leave no weighable residue; when 25 cc. oil are shaken with 5 cc. *spiritus conc.* and 2 drops of phenolphthalein solution, the alcoholic layer should assume a definite red colour when 0,3 cc. $^1/_{10}$ normal potash solution is added.

Chemical Preparations and Drugs.

Apiol. It will be remembered that this body has been introduced into the new French Pharmacopœia of 1908[1]) which is to come into force on 15th May of the current year[2]). For the present we have no means of estimating the total annual requirements of the French pharmacies in this article, but judging by the enquiries already received we are disposed to conclude that it is much in excess of the possible production. So far we have just managed to find enough raw material wherewith to produce the slight quantity of apiol for which a market could be found, but we greatly doubt if enough raw material will be available in case the demand for the article should increase materially. It would have been well if the editors of the Pharmacopœia in question had obtained sufficient information on this point beforehand.

Civet. We have received some few small lots of exceptionally fine quality, which we commend to the special notice of connoisseurs of this important perfume. We have in stock original horns of almost all sizes. Some parcels which were offered in Hamburg and Marseilles have turned out to be heavily adulterated, and it is particularly desirable to buy this article only from proved trustworthy suppliers, who are able to give satisfactory guarantees as to original quality.

Coumarin. Since the selling prices have been regulated by a syndicate, business runs a normal course, and although at the low prices ruling it is not possible to make large profits, the ruin which

[1]) Report November 1908, 144.
[2]) Compare the present Report, p. 8.

threatened to overtake this important perfume as a result of persistent price-cutting has been averted, at any rate for some time to come.

According to a report in the journal *Der Seifenfabrikant*[1]), the fruit of *Myrospermum frutescens* Jacq. (N. O. *Papilionaceæ*), which has an odour of coumarin and is used in Venezuela as a specific against rheumatism, yields, when extracted with ether, 47% of a viscid brown balsam, known as sereipo balsam. This balsam dries up rapidly, acquiring a resin-like appearance. Boiled with water, it yields a crystalline substance of the m. p. 207 to 208°, which was said to be coumaric acid. The saponified balsam boils at from 220° upwards, and decomposes during the boiling.

For the pharmacological behaviour of coumarin, see p. 115.

Menthol. We refer to the statements under the heading of Japanese peppermint oil on p. 78.

Musk, Tonquin. As a result of the scarcity of stocks towards the end of last season, the first arrivals of the new supply were being awaited with great impatience. These arrivals were placed upon the market as early as the month of November, and found buyers at good prices, in spite of their faulty quality. An improvement in the quality of the supplies occurred only in December, but "blue-skins", the most suitable kind for "graining", were almost entirely wanting. Every parcel which arrived at Shanghai, no matter what its classification, found ready takers at firm prices. France continues to occupy the first position as purchaser. The musk trade in Europe has gradually become centred in Paris and the figures given in the table below do not even approximately indicate the consumption in England and Germany, as only the direct shipments are recorded in it. A large part of the quantity given under the heading "Paris" ultimately finds its way to the two neighbouring countries.

Exports from Shanghai, from 1st January to 31st December 1908:

Year	To Paris	To London	To New York	To Germany and Austria	Total
	Catties	Catties	Catties	Catties	Catties
1908	666	37	211	9	**923**
1907	829	57	337	37	**1260**
1906	670	8	414	45	**1137**
1905	378	83	387	40	**888**
1904	722	76	366	52	**1216**

[1]) Der Seifenfabrikant **29** (1909), 61.

Safrol. The quotations for this important article have preserved their previous level during the last few months and, as heretofore, the principal share of the business has been concentrated in our hands. We can supply any quantity required, and in the case of large requirements we are always prepared to make special offers.

Thymol. No turn for the better whatsoever can be noted in the distressed condition of this important preparation. For the Hamburg firms, who have made it their business to ruin the article systematically, the condition towards which trade has been shaping is all the more unpleasant because ajowan seed has considerably declined in price, and large stocks of expensive material still remain to be worked up. We have succeeded in making very favourable purchases of seed in India, and shall be glad to submit to anyone interested in the article special offers for large parcels or for future delivery.

Notes on recent research work concerning terpenes and terpene derivatives.

General.

According to an article quoted from the *Bulletin mensuel de l'Office du Gouvernement Tunisien*[1]) the cultivation of essential oil yielding plants in Tunis has not attained that importance which properly belongs to it, because of the competition of Grasse and Germany, and also because heavy customs duties are levied in France on essential oils. Nevertheless, in the peninsula of Cap-Bon, especially at Hammamet and Nabeul, the natives grow geranium, tuberose and bitter orange on a small scale.

Pelargonium capitatum ("géranium rosat") is often cultivated for the manufacture of spurious rose oil. Oil prepared in a primitive manner sells at from 15 to 20 fr. per kilo, while if it is distilled in the proper way as much as 30, and occasionally even 40 fr. is paid for it. Cuttings cost about 2 fr. a thousand. The average cost of the necessary tilling of the soil is 40 fr., of the planting 35 fr., and of the working of the ground, which has to be done three times, 30 fr. The crops, which are gathered in April, August, and October, involve a total expenditure of about 90 fr. A hectare produces about 20 kilos of oil.

Orange flowers. For the preparation of neroli oil, the variety *bouquetier de Nice* is the most suitable. Petitgrain oil, which is worth little, is obtained by distilling the leaves. In Tunis the flowers are not distilled, but only sold. According to its age, a plantation containing 150 trees per hectare may produce from 2500 to 4000 kilos of flowers. These are bought up by distillers at 30 fr. or more, and on exceptional occasions at up to 50 fr. per 50 kilos. For some time past a French firm has been planting the *bouquetier de Nice* variety at Nabeul, while another firm buys the entire fresh flower crop there every year.

Acacia Farnesiana occurs in varieties with scented and with scentless flowers. Even in the dry districts it flourishes very satisfactorily. The plant requires only little water and hardly any attention, and so far as the quantity of flowers produced is concerned, its cultivation might yield a good supply for the perfumery industry.

Jasmine. *Jasminum grandiflorum* is preferred for the preparation of the perfume. The plant is grown from cuttings, which are placed at distances of $^1/_2$ m. The flowers are not distilled in Tunis, but they are an article of commerce, and sell at 2 to 3 fr. per kilo. In

[3]) Journ. de la Parfumerie et Savonnerie **22** (1909), 6.

a well-kept plantation the product is about 40 kilos of flowers per 1000 plants.

Eucalyptus. The distillation of eucalyptus leaves is practically not carried on at all, although, at any rate with *Eucalyptus globulus*, from 90 to 120 fr. per year per hectare might be realised.

Thyme. The oil is obtained from *Thymus algeriensis*, a familiar plant in Tunis, which grows rather thickly in the districts of Zaghouan, Pont-du-Fahs, Oudan, etc. The plant is distilled in a similar way to geranium and yields 1,5% of oil.

Mint. The oils are obtained by distillation of the leaves of penny-royal and peppermint. These two very hardy plants can easily be cultivated in Tunis and reed little care. 1000 kilos of leaves produce from 2 to 3 kilos of oil of a value of about 85 fr.(?) per kilo.

Tuberose. The tubers of *Polyanthes tuberosa*, N. O. *Liliaceæ*, are planted in rows at a distance of 30 cm. 1000 plants produce from 25 to 30 kilos of flowers, which sell at 2 to 2,50 fr. per kilo.

In 1907 Tunis imported 3423 kilos of essences and essential oils, to the value of 33122 fr.; the exports amounted to 14862 kilos, valued at 46127 fr.

Bibliography.

Otto Wallach, the well-known originator of modern terpene chemistry, has published the result of his 25 years' pioneering investigations in a comprehensive volume, entitled *Terpene und Campher. Zusammenfassung eigener Untersuchungen auf dem Gebiet der alicyclischen Kohlenstoffverbindungen*[1]). (Terpenes and Camphors. Repertory of my own Researches in the Domain of the Alicyclic Carbon combinations.) This work is by no means a mere reprint of every single treatise published by the author, who has written far more than a hundred such, but contains the whole material scattered throughout these publications, arranged systematically in review from uniform points of view.

In the general part of the work, Wallach first explains the principles upon which he has proceeded in his investigations, after which he deals with the mutual relations which he has found to exist between the separate members of the terpene series. In addition to the isomerisation processes, which are particularly characteristic of the series, all the numerous conversions which have been observed are recorded, arranged in tabular form as hydrocarbons, ketones, alcohols and oxides. Then follows an exposition of the methods of research which have been applied by Wallach with such extraordinarily prolific results. This section is divided into chapters on addition reactions in saturated and unsaturated combinations; reactions of interchange and abstraction;

[1]) Leipzig 1909, Veit & Co.

decomposition by oxidation, with notes on the specific behaviour of the various oxidising agents; reactions of condensation and ring-formation; and the rupture, and extension of ring-systems. After an exposition of the origin and behaviour of the most important types of combinations which are met with in practice, we have chapters on physical properties, constitutional relations, syntheses, division and nomenclature. An extensive review of all the combinations which have been examined, systematically arranged, and containing accurate and complete references to the literature of each combination, brings the general part of the work to a close.

The second, or "special" section contains, in concise form, the vast positive experimental material dealt with in Wallach's publications. This is arranged in the 19 principal groups which have, in practice, served as bases of investigation, viz., Pinene, Pinol, Limonene, Terpinolene, Terpine and Terpineol, Cineol, Carvone, Eucarvone, Pulegone, Menthone, Monocyclic Ketones, Terpinene, Phellandrene, Sylvestrene, Sabinene, Thujone, Fenchone, Camphor, and Sesquiterpenes. Each of the principal divisions in this section is preceded by an introductory chapter giving a brief general review of the particular field covered.

Wallach's work affords ocular demonstration of the wideness of the field which this famous investigator has thrown open to scientific research, and also shows how large a share he has had in its development. It will be of special interest and great usefulness not only to his pupils, to whom it is dedicated, but to all other workers in this branch of science.

The third part of the second volume of the third edition of *Posts Chemisch-technische Analyse* which has been edited by B. Neumann, contains a chapter on essential oils by J. Helle. The author first describes briefly the manner of testing the raw materials and then enters in detail into the physical and chemical testing of essential oils, in the course of which, besides dealing with the generally applicable methods, he considers a few special processes, such as, for example, the determination of cineol, hydrocyanic acid, isothiocyanallyl, etc. The detection of the most common adulterants is also discussed at length. A tabular review of the properties and composition of the principal essential oils brings this little work to a close. The book will no doubt prove a good and reliable guide for technical chemists in the analysis of essential oils.

A second edition of Ernest J. Parry's well-known work *The Chemistry of Essential Oils and Artificial Perfumes* has been published (Scott, Greenwood & Son, London, 1908), with the object of recording

the progress which has been made in the investigation of essential oils since the first appearance of the book in 1899. The enormous output of publications dealing with essential oils has necessitated a considerable enlargement of the book, which finds expression in the growth of the volume up to 546 pages, as compared with 411 pages in the first edition. The work concerns itself chiefly with laboratory practice, and for this reason it deals only briefly with the chemistry of the various constituents and the method of preparation of the oils, while on the other hand a great deal of space is devoted to the description of the properties and to the testing of oils. The leading commercial oils in particular are discussed at great length, special stress being laid upon the detection of adulterations and upon the eventual quantitative determination of the constituents, which are of value in determining the value of each particular oil. The book contains, for example, detailed information with regard to the determination of citral, cinnamic aldehyde[1]), eugenol, cineol, etc. A special chapter is devoted to artificial perfumes. As an appendix to the book there is a chart indicating the specific gravity, rotation, index of refraction and composition of the principal oils, and another showing the requirements of the various Pharmacopœias with regard to essential oils.

Although in certain details we are of different opinion as Mr. Parry, his book must nevertheless be pronounced as, upon the whole, a sound guide for the chemist who is engaged in the investigation of essential oils, and in its new dress it ought to add fresh friends to its old circle.

In a brochure entitled *Les constituants des Huiles Essentielles* (Paris, Alph. Isnard) the author, Marcel Viard[2]), treats his subject in a concise, summary manner. After a discussion on the general properties of essential oils, with consideration, in parts, of the effect thereon of their chemical composition (which discussion may be regarded as a sort of introduction), Viard first proceeds to draw a general outline of the methods used in the separation of the most important constituents of the oils, and then refers specially to the separate bodies, which he groups according to their chemical properties. In the case of each combination reference is made to the oils which serve as the crude material for its preparation, and methods are given for the quantitative determinations of the oils, insofar as any are known, as well as for the manner of isolating the constituents of the various oils. In the case of the more important combinations there are also data for the purification of the crude product. Viard further gives data for judging the various bodies,

[1]) Parry calls our cassia flask "Hirschsohn flask". Compare Report November 1908, 92.

[2]) We here return thanks to Mr. Viard for courteously sending us a copy of his pamphlet.

the properties and derivatives of which he discusses. This small monograph, which has been written by a practicist, should be of special interest to those practically engaged in the business.

The Commercial Products of India (London, John Murray, 1908) is the title of a book by Sir George Watt which, as the author himself states, consists of a synopsis of his own voluminous work *Dictionary of the Economic Products of India.* It goes without saying that in this synopsis regard has been taken to recent research. The volume, which contains 1189 pages, carries out its purpose of giving, in a compressed and concise form, the most important details on the economic products of India. It will probably be welcomed by all who wish to acquaint themselves rapidly with what is most worth knowing on this subject.

We are glad to seize this occasion of expressing our best thanks to the author for kindly presenting us with a copy of the book.

A further series has appeared of J. W. Brandel's[1]) discussions on the investigations of essential oils published in the years 1901 to 1903, to which work we have repeatedly referred in the past[2]).

Analytical.

The method for the determination of the citral content in oil of lemon by the use of hydroxylamine, which was recommended by J. Walther[3]) and discussed by us in detail at the time[4]), has now been published, in a modified form, by A. H. Bennett[5]). This author uses potash liquor instead of bicarbonate of sodium for averting the evolution of carbonic acid and the loss of hydroxylamine which may result therefrom. The quantity of alcoholic potash used by him is sufficient to liberate from its hydrochloric salt an excess of hydroxylamine in proportion to the citral present, so that a residue of unconverted hydrochloride is left. Bennett proceeds as follows: He dilutes a mixture of 20 cc. of lemon oil and 20 cc. alcoholic (80 per cent. alcohol) $^1/_2$ normal solution of hydrochloride of hydroxylamine with 8 cc. of alcoholic normal alcoholic potash and 20 cc. strong alcohol, free from aldehyde, and boils for half an hour with reflux-condenser. After cooling, the mixture is diluted with 250 cc. water, part of which is used for washing down the reflux-condenser, and the hydrochloric acid which is still present in the form of hydrochloride of hydroxylamine

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[1]) Pharm. Review **26** (1908), 371.
[2]) Report April **1908**, 168; November **1908**, 155.
[3]) Pharm. Zentralh. **40** (1899), 621; **41** (1900), 614.
[4]) Report April **1900**, 22.
[5]) The Analyst **34** (1909), 14. Quoted from Chem. Zentralbl. **1909**, I. 593.

is neutralised, phenolphthalein being employed as indicator. The hydroxylamine which is not in combination with citral is then titrimetrically determined with $^1/_2$ normal sulphuric acid by ascertaining the final reaction by means of stipple-tests with a very dilute methyl orange solution. A similar course is followed in a blank test without oil of lemon, in order to determine the value of the hydroxylamine solution. The quantity of hydroxylamine which has entered into reaction is calculated from the difference in the cc. of $^1/_2$ normal sulphuric acid which has been used up in each of the tests, and furtheron, the amount of citral, by multiplying by 0,076. A. H. Bennett has tested the value of the method with pure citral; in the case of oils of lemon the citral content thus determined varied from 4,3 to 5,2 %.

We were unfortunately unable to form an opinion as to the method in time for the present Report, and we therefore limit ourselves here to a mere recapitulation of the process. We shall return to the matter in our next Report.

A method for the colorimetric determination of benzaldehyde in extracts of bitter almonds, which resembles Mac Kay Chace's method for the determination of citral previously discussed by us[1]) has been described by A. G. Woodman and E. F. Lyford[2]). The solution of fuchsin-sulphurous acid required for this purpose is prepared fresh each time in the following manner: 0,5 g. fuchsin is dissolved in water, and sulphurous acid introduced into the solution until the weight has increased by 20 g. when it is further diluted to make 1 litre. In the next stage, alcohol free from aldehyde is employed; this is obtained by taking spirit which has undergone a preliminary treatment with oxide of silver, and diluting it with 25 g. phenylene diamine hydrochloride per litre of alcohol, then passing a strong current of air through it for three hours, and distilling off, rejecting the first 100 cc. Besides this, a standard solution of freshly distilled benzaldehyde in aldehyde-free alcohol (1 mg. in 1 cc.) is prepared. Next, 10 g. of the almond extract are diluted to 50 cc. with aldehyde-free alcohol; 2 cc. of this solution is placed in a colorimeter tube and diluted to 20 cc. Three control-solutions containing respectively 2, 4 and 6 mg. benzaldehyde are then poured into tubes of equal size, all the tubes are brought to a temperature of 15°, the contents quickly diluted with 20 cc. of the fuchsin-sulphurous acid solution, shaken up, and allowed to stand for 10 minutes. As much of the sample-solution is now run off as will make its colour resemble that of one of the control-solutions. As the colour is in proportion to the degree of concentration of the

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[1]) Report April **1907**, 116.
[2]) Journ. Americ. chem. Soc. **30** (1908), 1607.

benzaldehyde, the proportion of that body which is present may be calculated. The method is said to give accurate results, and to be applicable also to bitter almond oil.

In a paper read by S. H. Baer[1]) before the Association of Official Agricultural Chemists on November 8th 1908, the author points out that there is no practical method for the analysis of "terpeneless lemon extract" based upon the determination of the citral content, and that consequently an unobjectionable method for fixing standard values for the product in question is rendered very difficult. Officially a content of at least 0,2 % of citral, which must be obtained from oil of lemon, is demanded. As for analytical investigations commercial citral, obtained from lemongrass oil, is mostly used, Baer thinks it desirable that citral from oil of lemon should be taken as the basis for analytical investigations, especially because citral may exist in isomeric forms. Baer goes on to criticise some of the methods proposed for the determination of citral. As the most suitable method he regards one in which the distilling-off of alcohol and water is obviated and in which the small quantities of citral could be separated from the highly diluted aqueous alcoholic solution by means of a solid derivative for gravimetric determination. For this purpose the bisulphite compound or the semicarbazone might perhaps be used. According to the tests carried out by Baer, Chace's method[2]) is unsuitable in practice, if only because in manufacturing processes the application of chemically pure citral, distilled water, and alcohol free from aldehyde, is of course out of the question. Besides this, it would be impossible to detect any adulteration with other aldehydes, such as acetaldehyde. On these grounds, Baer opposes the official adoption of Chace's method.

On a method for the determination of thujone in liqueurs, see oil of Wormwood, p. 92.

Physical notes.

J. W. Brühl[3]) has tested instances in which hydrocarbons with conjugated ethenoid-linkings do not show the condition known as "exaltation". As terpinene, which was recognised by Wallach[4]) as a mixture of $\Delta^{1,3}$- and $\Delta^{1,4}$-dihydrocymene, showed a normal molecular refraction, whereas the $\Delta^{1,3}$-dihydrocymene prepared synthetically by

[1]) American Perfumer **3** (1909), 205.
[2]) Journ. Amer. chem. Soc. **28** (1906), 1472; Report April **1907**, 116.
[3]) Berl. Berichte **41** (1908), 3712.
[4]) Liebig's Annalen **362** (1908), 293; Report November **1908**, 174.

Harries and Majima[1]) showed "exaltation", Brühl expresses the surmise that it is in the well-known faculty of rearrangement of the cyclic unsaturated hydrocarbons that the cause must be sought of the anomalies which have been observed. He furthermore extends his theoretical speculations to recent publications by Auwers and Hesseland[2]) and also by Zelinsky and Gorsky[3]). We cannot go into details on the subject here; suffice it to state that in the case of aliphatic compounds through the conjugation of the ethenoid-groups an "exaltation" of molecular refraction and molecular dispersion was invariably observed, the conjugations increasing in number in an ascending degree. According to Brühl the molecular dispersion in particular is a prominent criterion of the constitution.

Pharmaco-Physiological Notes.

E. Rimini and F. Delitala[4]) have carried out pharmacological researches with safrol, myristicin, apiol, and asaron and with their corresponding propenyl combinations and β-nitro-derivatives. All these combinations acted upon the central nervous system of cold-blooded as well as of warm-blooded animals. In the case of the former, small doses of the allyl and propenyl combinations had a marked narcotic effect, while the β-nitroderivatives provoked a characteristic condition of muscular rigidity. Larger doses produced increasing symptoms of paralysis, ending in death. The allyl combinations had the strongest, the β-nitro-derivatives the weakest, toxic effects; the propenyl combinations stood midway between these two. Safrol possessed the greatest toxicity, β-nitro isoapiol the smallest. These differences in behaviour are to be explained by the greater or less absorbability of the substances concerned. In the case of warm-blooded animals internal administration produced vomiting. When hypodermically administered, the liquid substances produced acute, and the solid substances chronic, intoxication, followed in both cases by fatal results. We are unable to enter into details of the investigations here, and for these we refer to the original paper.

J. Hämäläinen[5]) has made experiments on the action of d-, r- and l-camphor on the heart of the frog, which showed that all three of these modifications were almost without effect upon that organ, of

[1]) Berl. Berichte **41** (1908), 2516; Report November **1908**, 175.
[2]) Berl. Berichte **41** (1908), 1819.
[3]) Ibidem 2479, 2630.
[4]) Archivio di Farmacologia e Terapeutica **14** (1908), 295. From a copy kindly sent to us.
[5]) Skandinavisches Archiv für Physiologie **21** (1908), 64. We quote from a copy kindly sent to us.

which the frequency and power of contraction are almost normal. Upon a heart influenced by chloral, d- and r-camphor had an almost equal action, in which the activity of the heart was often permanently excited. Both were also able to remove the condition of inactivity caused by chloral. On the other hand, l-camphor generally produced only a weak excitation of short duration, while in a few instances the action of the heart was improved by the other modifications. The condition of inaction caused by chloral could not be counteracted by l-camphor. In connection with this matter we call attention to the experiments of Langgaard and Maass on the same subject, which we have referred to in one of our earlier Reports[1]).

Several investigations have been made of late years into the narcotic action of nutmegs[2]). F. Jürss in particular, in his paper *Über Myristicin und einige ihm nahestehende Substanzen* (On myristicin and a few allied substances), published in 1904, called attention to the peculiar fact that from 10 to 12 g. of nutmeg oil or mace oil are required in order to produce toxic symptoms in rabbits, whereas a single nutmeg weighing from 4 to 5 g. is sufficient to cause severe symptoms of this kind in man. It had been ascertained that the myristicin which is present in the oil has a toxic action, affecting in particular the liver, its action upon that organ often causing fatty degeneration, as in the case of phosphorus-poisoning. But the proportion of myristicin in nutmegs is so small that their powerful narcotic action must possibly be due to the presence of another constituent. In order to shed light upon this problem, F. B. Power and A. H. Salway have made a most thorough study of the constituents of the nutmeg. We have already on a previous occasion[3]) reported on the results obtained by them in respect of the essential oil. Further communications by these two authors have now appeared, dealing with the constitution of nutmeg oil obtained by pressure[4]) and of the pressed cake[5]). These communications are completed by numerous physiological experiments carried out by H. H. Dale. We do not propose to enter into details here, but will only state that no alkaloids or proteïnic substances possessing a toxic action were traced. The chief outcome of the investigations has been the determination of the fact that the narcotic properties of the nutmeg are certainly due to myristicin. It may be inferred from this that myristicin is more easily assimilated when in combination

[1]) Report April **1908**, 176.
[2]) Compare Report April **1908**, 76; November **1908**, 161.
[3]) Report April **1908**, 74.
[4]) Journ. chem. Soc. **93** (1908), 1653.
[5]) Americ. Journ. Pharm. **80** (1908), 563.

with other constituents of the nutmeg than in the pure state, and this theory would explain the differences in the behaviour of the oil and of the nutmeg. The lower animals were much less susceptible to the direct action of nutmeg upon the functions of the brain than were human beings. This agrees with the result of observations on other bodies possessing a narcotic action.

The thiozonide of linalyl acetate prepared by H. Erdmann, and referred to in our last Report[1]) has been employed by F. Nagelschmidt[2]) in clinical experiments in cases of psoriasis, cystitis, syphilis and scabies. These experiments showed the thiozonide to be decidedly superior to thiopinol, the solution of sulphur in oil of pine-needles which had formerly been the subject of experiment. The organic combination of the sulphur appears greatly to increase the power of absorption by the skin when the preparation is administered in the form of an ointment or in the bath. Other advantages of the remedy are its agreeable odour, its non-irritant properties, and the possibility of administering it in exact doses. It was used in various forms, such as an alcoholic solution of organic linalyl acetate thiozonide of sodium together with anorganic sodium thiozonate ("thiozone"), in some instances mixed with glycerine, or as a solution in oil of lavender of the pure thiozonide. Details of the cases treated show the effect of the preparation on the separation of sulphuric acid in the urine. From these records it appears that there was a regular and well-defined increase in the total amount of sulphuric acid separated in the urine, while the total amount of sulphur only increased in proportion to the increase of the sulphuric acid.

A. Ellinger[3]) has ascertained that coumarin, in proper doses, is a useful narcotic for frogs and rabbits, and, in experimental investigations, possesses the advantage of influencing the circulation only very slightly. On the other hand, it proved to be unsuitable for dogs and for man. For details see the original work.

Observations on the symptoms caused by the self-administration of 8 g. of menthol have been made by A. Schwenkenbecher[4]). The familiar prickly sensation of cold in the mouth and throat extended downwards to the œsophagus to the limit of the presence of nerves susceptible to cold; it therefore ceased in the intestinal

[1]) Report November **1908**, 178.
[2]) Therap. Monatshefte **22** (1908), 520.
[3]) Archiv f. exp. Pathol. u. Pharmak. **1908**. Suppl.: Schmiedeberg-Festschrift. Quoted from Chem. Zentralbl. **1908**, II. 1945.
[4]) Münch. med. Wochenschr. **1908**, No. 28. Through Therap. Monatsh. **23** (1909), 58.

canal. Finally the sensation of cold was also transferred to the mucous membrane of the nose and even to the cuticle, but no change of the circulation in the cellular tissue of the skin was observable. It follows that menthol excites the extreme parts of the nervous organs susceptible to, or capable of, transmitting cold, wherever it comes in contact with them.

It has been repeatedly observed that the oil of *Umbellularia californica* Nuttall possesses a pungent odour which stimulates the action of the lachrymal duct, and also produces headache, and it has further been discovered[1]) that these unpleasant effects are due especially to the fractions containing umbellulone, a substance which has recently been examined in detail. We have also had occasion lately to observe the action mentioned above when preparing umbellulone, and at our request Prof. R. Kobert, of Rostock, has examined this ketone pharmacologically. We are indebted to the Professor for the following report on the result of his investigations: —

"The action of umbellulone was tried both on warm-blooded and on cold-blooded animals. With frogs it has a central paralysing action upon the nervous system. A 0,05 g. dose suffices to paralyse medium-sized, vigorous specimens of *Rana esculenta* within 15 minutes, causing them to lie prone as if in death and to be irresponsive to any excitants. But the motoric nerve cylinders continue to be responsive to the electric current, and the heart continues to beat for several hours, when its action slowly ceases. A dose of 0,025 g. also induces complete paralysis, but in this case recovery takes place after an interval of some hours. Neither large nor small doses produce convulsions. 1 g. of umbellulone injected into a small rabbit weighing 570 g. produced symptoms resembling intoxication in the course of 15 minutes. After a further interval of 10 minutes it lay as if in a profound sleep and was almost irresponsive to excitants. At first respiration and cardiac action continued normal. 40 minutes after the injection the respiration and the beating of the heart grew fainter and 50 minutes after the injection the animal died without any symptoms of excitation. This experiment led to the idea of using umbellulone as a narcotic, and a much smaller dose was tested for possible subsidiary effects. As small a dose as 0,4 g. per 1500 g. rabbit (hypodermically) produced dislike for food lasting several days and albumen in the urine. In contact with blood-corpuscles, umbellulone causes hæmolysis, even when greatly diluted. In view of these facts the use of umbellulone in therapy is probably out of the question."

[1]) Heany, Americ. Journ. Pharm. **47** (1875), 105; Pharmaceutical Journal III. **5** (1875), 791; Stillman, Berl. Berichte **13** (1880), 630; Power and Lees, Journ. chem. Soc. **85** (1904), 629. Report October **1904**, 87.

Prof. Kobert reserves further investigations (especially as regards the question to what extent the action of umbellulone in cases of acute poisoning may resemble that of pulegone in causing pronounced organic changes, akin to those caused by phosphorus poisoning) and also comparative tests in respect of its antiseptic properties.

For notes on the pharmaco-physiological behaviour of p-, m-, and o-thymol, see p. 136.

Phyto-physiological Notes.

Reference may here be made to a lengthy treatise by O. Tunmann[1]) entitled "Contribution to the knowledge of the cuticular glands", because some volatile oils owe their existence to these glands. The author discusses in the first place the essays dealing with the forming of secretions, and concludes that there is a correspondence between the formation of secretions in the vegetable Kingdom and the same process in the glandular tissues of the human skin, that is to say, the sebaceous glands and gland-surfaces. The secretive matter is only found outside the glandular cells, as it is divided from the plasma of the secernating cells by a wall of cellulose which is always visible. As it has been proved that the secretion occurs only in the subcutaceous gland-sacs, it must have originated there, and must have been produced by a resin-secreting membrane. The first investigator who discovered the resin-secreting layer was Tschirch, who gave to this part of the membrane the name of "resinogenous layer" (resinogene Schicht). The determination of this layer in the glands of the skin is easier when the material worked upon has been soaked for one or two months in concentrated aqueous solution of acetate of copper, which hardens it. If fresh material is employed, the *modus operandi,* according to Tunmann, should be as follows: Delicate horizontal cuts should be made, so that the glands may be inspected from above, or in diagonal section. Next add an aqueous solution of chloral hydrate (10, 20, 30 or 40%). If the layer should not yet be visible the strength of the solution should be increased by degrees until the major part of the resin has been dissolved. Now exert with the finger a gentle pressure upon the side of the covering glass. This will burst the cuticle and push it aside, while the resinogenous layer will be placed either upon the top of the secernating cells, or, separated from the latter, at the side of the gland-head. It is not necessary that all the resin should be dissolved. Staining with diluted tincture of alkanet will show the residual resin, leaving the resinogenous layer uncoloured.

[1]) Berichte d. deutsch. pharm. Ges. **18** (1908), 491 to 540.

It is very easy to find the layer in dried vegetable material (drugs). In a few cases the cuticle will here be found to have burst, and the secretion to have run out, the layer being thus disclosed without further trouble; in other cases it is necessary to use chloral hydrate solution, as mentioned above.

By the aid of the processes described, Tunmann succeeded in discovering the resinogenous layer in all the plants examined by him. In the course of his investigations he was able to determine various typical forms of the layer. These he divides into three principal types: the rod-type (*Viola, Fraxinus, Alnus*), the vacuola-type (*Salvia, Hyssopus*) and the mesh or grille type (*Rhododendron, Azalea*).

The cuticle of the glands of the skin is partly enlarged by stretching, partly by subsequent development. Its principal purpose is unquestionably to prevent a too rapid exudation or loss of the secretions. In the case of all the persistent glands of the *Labiatæ, Pelargoniæ, Compositæ* etc., all of which possess a strong cuticle, a continuous volatilisation of essential oil takes place throughout the whole life of the plant, that is to say, a loss of the volatile portions of the secretion by way of the cuticle. In the course of this process the chemical composition of the essential oil must of course undergo some modification, but it does not reach a demonstrable process of resinification, because new volatile portions are continuously being formed. Only in autumn, when the period of growth is reaching its end, this formation of volatile constituents ceases, and the remainder of the oil resinifies. Thus it is that autumnal leaves are found to contain in lieu of the usual, almost colourless, highly refractory essential oil, a dark yellow, partly crystalline, partly amorphous, somewhat sparingly soluble lump of resin.

Generally speaking, the view has been accepted that vegetable secretions are decomposition products formed in the course of the metabolism, but Tschirch breaks a lance for the theory that these secretions are built up to serve quite definite and various biological objects, and in this view he is supported by Tunmann.

In some cases, the formation of essential oil in the plant begins at a very early stage, in fact, before the gland has attained its full development.

In opposition to Charabot, Tunmann shows that the constant change in the chemical composition of vegetable essential oils during the progress of the development of the plant, is chiefly due to the continuous evaporation of the more volatile parts. He agrees with Charabot in deducing, from pharmaco-physiological considerations, that plants in flower cannot yield so valuable an oil as can the young spring leaves.

Hydrocarbons.

Ocimene. C. J. Enklaar has subjected ocimene (the aliphatic hydrocarbon which had already been examined by him several times) [1]), and some of its derivatives, tho the action of ozone.[2]) When ocimene was ozonised in carbon tetrachloride solution there was formed an oily ozonide of variable composition, possessing the properties of an aliphatic ozonide. In addition there were formed products of decomposition, which either separated out in the form of a sublimate, or were kept in solution by the carbon tetrachloride. They were partly of a crystalline, partly of a liquid, constituency. The liquid products of decomposition appeared to consist of methylglyoxal; the solid products were made up of trioxymethylene (m. p. 164 to 166°), the polymer of formaldehyde, and of acetone peroxide (m. p. 131°). When allo-ocimene was ozonised, trioxymethylene and acetone peroxide were likewise obtainable, but in this case the ozonide itself appeared to be a combination containing less than 10 carbon atoms. Dihydro-ocimene, $C_{10}H_{18}$, yielded an oily ozonide which was soluble in carbon tetrachloride, but insoluble in petroleum ether. The single ozonides were decomposed by water, in the course of which process ocimene and allo-ocimene ozonides gave off dioxide of carbon. The aqueous solution of the products of decomposition of ocimene ozonide contained a polymer of methylglyoxal (as was shown by a conversion into the proper substance), of which the phenylhydrazone melted at 145°. Furthermore, the presence of acetone, acetic acid and malonic acid could be proved. Probably, malonic aldehyde had also been formed, the pronounced red coloration which was given with ferric chloride, and the formation of a semicarbazone melting at 245°, pointing to this conclusion. On the other hand, no lævulic acid, oxalic acid, or lævulic aldehyde could be detected. The following decomposition products of allo-ocimene had been formed: acetone, an aldehyde (phenyl hydrazone, m. p. 230°), pyroracemic acid (phenyl hydrazone, m. p. 169°), and very probably also malonic aldehyde. The ozonide of the dihydro-ocimene yielded as products of decomposition principally lævulic acid (b. p. 148 to 149° at 14 mm. pressure); also acetone, acetic acid and probably lævulic aldehyde and malonic aldehyde. A determination of the molecular dispersion of the three above-named hydrocarbons showed considerable deviations from the values calculated.

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[1]) Report October **1904**, 14; April **1906**, 109; October **1907**, 113; November **1908**, 153.

[2]) Recueil des trav. chim. des Pays-Bas **27** (1908 422. From a copy kindly sent to us.

Pinene. By oxidation of d- and l-pinene of high rotatory power, Ph. Barbier and V. Grignard[1]) obtained the optically active forms of pinonic and pinic acids. l-Pinene from French turpentine oil (b. p. 155 to 157°, α_D — 37,2°; 157 to 160°, α_D — 32,3°) was oxidised with permanganate. From the product of oxidation, which (after elimination of the volatile acids and of nopinic acid) boiled at 189 to 195° under 18 mm. press., l-pinonic acid separated out in long crystalline needles, which, after filtration by the suction pump and re-crystallisation from a mixture of ether and petroleum ether, melted from 67 to 69°. The acid was easily soluble in water and ether, fairly soluble in chloroform, and almost insoluble in ligroin. Its specific power of rotation was determined to be $[\alpha]_D$ — 90,5° in chloroform solution. Oximation produced two oximes; one lævogyre, m. p. 128°; and the other dextrogyre, m. p. 189 to 191°, corresponding to the β- and γ-pinonic acid oximes described by v. Baeyer[2]), which this investigator obtained from oily pinonic acid. By oxidising l-pinonic acid with hypobromite, active pinic acid, $C_9H_{14}O_4$, was produced. This possessed the following characteristics: b. p. 225° at 17 mm. press., m. p. 135 to 136°, $[\alpha]_D$ + 7,10° in acetone solution. The oily parts filtered off from l-pinonic acid proved to be a mixture of this acid with racemic pinonic acid, the latter melting at 104 to 105°.

d-Pinene from myrtle oil (b. p. 155 to 158°; $d\frac{14°}{4°}$ 0,8635; n_D 1,46977; $[\alpha]_D$ + 39,4°) yielded upon oxidation a mixture of racemic and d-pinonic acids. The latter melted at 67 to 68° and showed the same properties as the acid described above, except as regards its specific rotatory power, which was found to be $[\alpha]_D$ + 89,0°. By mixing the two active pinonic acids the inactive form, m. p. 104°, was obtained. Oximation produced the two oximes corresponding to the above. A preparation obtained by Tiemann from α-dihydroxy dihydrocampholenic acid by means of distillation, and described as l-pinonic acid (m. p. 98 to 99°; oxime m. p. 147°) possibly represents, according to Barbier and Grignard, a stereo-isomeric acid.

With reference to the foregoing we wish to point out that research upon the same subject has been in progress in our laboratory. We were the first to obtain l-pinonic acid by oxidation of l-pinocamphone from oil of hyssop, and described it briefly in a preliminary communication[3]).

We had reserved further investigation of the compound to ourselves. In order to place beyond a doubt the characteristics of our acid by comparing it with the dextrorotatory acid, and inspired by the same con-

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[1]) Compt. rend. **147** (Oct. 5, 1908), p. 597.
[2]) Berl. Berichte **29** (1896), 2786.
[3]) Report April **1908**, 58. Chem. Zentralbl. **1908**, I. 1840. May 20.

siderations upon which Barbier and Grignard proceeded, we had oxidised a pinene of high rotatory power from Greek turpentine oil (b. p. 156°; $d_{15°}$ 0,8642; $n_{D20°}$ 1,46565; $[\alpha]_D$ + 47,73°) and had likewise obtained d-pinonic acid. The constants ascertained by us for both acids agree with the indications given by Barbier and Grignard. For the lævogyre acid we found: m. p. 69,5 to 70° and $[\alpha]_D$ — 90,36° in chloroform solution; for the dextrogyre acid: m. p. 68 to 69° and $[\alpha]_D$ + 88,2° in the same solvent. We purpose, later on, to publish elsewhere our investigations into these bodies.

According to P. Golubew[1]), pinene nitroso-chloride, by treatment with piperidine, can be made to yield, besides the nitrol-piperidide (m. p. 118 to 119°), nitroso-pinene (m. p. 134 to 135°) by the splitting off of hydrogen chloride. As Wallach[2]) showed long ago, the reaction, when other bases, such as diethylamine, are used, takes place chiefly in the last-named direction.

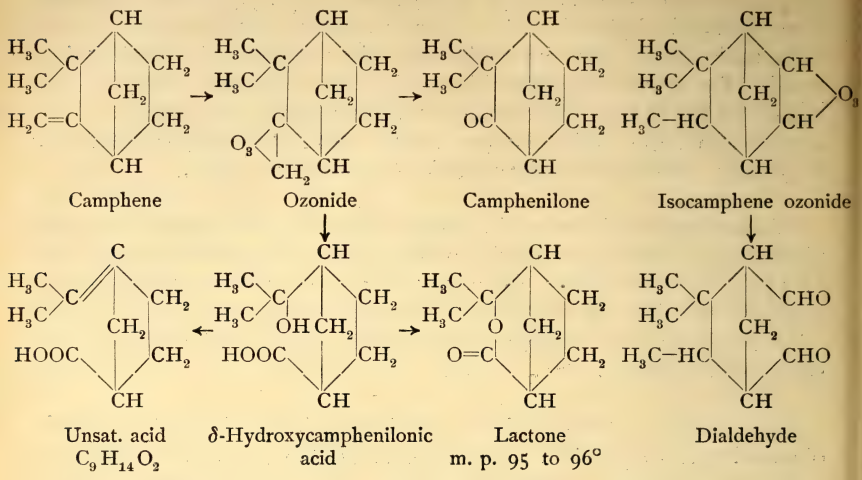
Camphene. While oxidising crude camphene, F. W. Semmler[3]) obtained practically only a single oily ozonide $C_{10}H_{16}O_3$, which, however, could be split up in two different ways. In one case it yielded 30% of camphenilone $C_9H_{14}O$ (m. p. 40°; $d_{38°}$ 0,9705; semicarbazone, m. p. 223°) of which the oxime (m. p. 109°; b. p. 128 to 129° at 14 mm. press.) was converted through the nitrile into camphoceenic acid (b. p. 145 to 146 at 11 mm. press.; $d_{20°}$ 1,020; n_D 1,4862). By the other method there was obtained from the ozonide a syrupy saturated hydroxy acid $C_9H_{16}O_3$ (δ-hydroxycamphenilonic acid) which by means of distillation *in vacuo* was converted into an also saturated, well-crystallising lactone $C_9H_{14}O_2$ (m. p. 95 to 95°; b. p. 126 to 128° at 10 mm. press.). In addition to the above method, the process of splitting-off of water could be carried out in another way, resulting in a mixture of a saturated and a non-saturated acid, both of them possessing the formula $C_9H_{14}O_2$. Now, the formation of camphenilone from semicyclic camphene can be understood without further explanation, but the formation of the hydroxy acid, that is to say of the lactone, can only have resulted from ring-disrupture. As, moreover, no dialdehyde could be isolated from the products of decomposition of the crude ozonide, Semmler believes that the hydroxy acid, and also the lactone, are not formed from the cyclic-unsaturated isocamphene but also from the semicyclic camphene, which must consequently form the chief constituent of the crude camphene. Ozone did not react in any way

[1]) Journ. russ. phys.-chem. Ges. **40** (1908), 1015. Quoted from Chem. Zentralbl. **1908**, II. 1865.

[2]) Liebig's Annalen **245** (1888) 254.

[3]) Berl. Berichte **42** (1909), 246.

with camphenilone or fenchone. Semmler gives the following formulœ for the separate processes: —



Terpinene. F. W. Semmler[1]) has made a critical study of the statements recorded relating to terpinene obtained by various different methods. He calls attention to the fact that there is a series of contradictory statements on this subject, especially as regards the exaltation which has been observed, and the formation of the nitrosite. His experiments, which are described below, point the way towards a clearing-up of this involved condition of things, but the results obtained do not even now permit of any certain conclusions to be drawn. By treating carvenone with pentachloride of phosphorus, without application of heat, Semmler obtained a monochloride of carvenene, $C_{10}H_{15}Cl$, which was converted into carvenene, $C_{10}H_{16}$, by reducing it with sodium and alcohol. This body possessed the following constants: b. p. 179,5 to 180,5° at 735 mm. press., 61 to 63° at 10 mm. press., $d_{20°}$ 0,844, n_D 1,491, molec. refraction, found 46,74, calculated for $C_{10}H_{16}/\overline{2}$ 45,24. According to its origin, this hydrocarbon should be $\Delta^{1,3}$-dihydrocymene, and might therefore be identical with terpinene[2]). But, in contradistinction to the observations which have been made on terpinene, carvenene showed an exaltation of about 1,5. On the other hand it gave the nitrosite reaction, although not very readily. This experiment shows that conjugated cyclic linkings may cause exaltation.

Up to the present no inversion had been observed in the treatment of terpinene with acids. But when carvenene was boiled for two

[1]) Berl. Berichte **41** (1908), 4474; **42** (1909), 522.
[2]) Compare Report November **1908**, 175.

hours with 25% alcoholic sulphuric acid, it yielded a hydrocarbon which Semmler calls isocarvenene, and which he regards as $\Delta^{1,4}$-dihydrocymene. Among its constants (b. p. 59 to 62° at 10 mm. press.; $d_{20°}$ 0,845; n_D 1,480, exaltation about 0,4), the value of the refraction especially differs from that observed in the case of carvenene. In addition to the product described above, a diterpene had been formed, which has been called dicarvenene and which possessed the following constants: b. p. 170 to 173° at 10 mm. press., $d_{20°}$ 0,928, n_D 1,5175, molec. refr. found 88,8, calculated for $C_{20}H_{32}/\overline{2}$ 87,07, for $C_{20}H_{32}/\overline{3}$ 88,77. It is somewhat remarkable that the isocarvenene also appeared to yield terpinene nitrosite, and no satisfactory explanation of this occurrence is given. As a combination with two adjacent double linkings, carvenene passed over, on treatment with sodium in amyl alcoholic solution, (although only slowly), into Δ^2-tetrahydrocymene. For the last-named body the following constants were found: b. p. 55 to 56° at 12 mm. press., $d_{20°}$ 0,824, n_D 1,461. The ozonide of carvenene, when decomposed with water, yielded dimethyl acetonyl acetone, (b. p. 82 to 86° at 10 mm. press., $d_{20°}$ 0,95, n_D 1,433) of which the dioxime had a melting-point of 130°. The terpinene preparation obtained by the familiar methods, on the other hand, yielded only very little of this diketone. In the terpinene which was obtained from terpinene dihydrochorate by splitting-off hydrogen chloride Semmler was, moreover, able to prove the existence of a large quantity of terpinolene by means of the bromide, melting at 117°.

Isocarvestrene. In a manner similar to that in which, some time ago, Perkin and Tattersall[1]) carried out the synthesis of carvestrene, W. H. Perkin jun. and K. Fisher[2]) have now succeeded in preparing an isocarvestrene ($\Delta^{6,8(9)}$-m-menthadiene).

1-Methylcyclohexane-6-one 3-carboxylic acid (m. p. 94 to 96°; oxime, m. p. 172°; semicarbazone, m. p. 200°) yielded by reduction with sodium amalgam a mixture of cis- and trans-1-methylcyclohexane-6-ol 3-carboxylic acid. The cis-acid had m. p. 141°, it yielded a lactone of m. p. 46° and when treated with hydrogen bromide was converted into cis-6-bromo 1-methylcyclohexane 3-carboxylic acid (m. p. 53°). The trans-hydroxy-acid melted at 115 to 117° and yielded an oily brominated acid. The mixture of the two bromo acids was esterified, whereupon hydrogen bromide was split off by means of diethyl aniline, resulting in the formation of the ester of 1-methyl Δ^6-cyclohexene 3-carboxylic acid, boiling at 146° under 100 mm. press. The b. p. of the free acid under the same pressure was about 184°. Upon treatment of the ester with magnesium methyl iodide, dihydro isocarvestrenol

[1]) Journ. chem. Soc. **91** (1907); Report April **1907**, 145; October **1907**, 146.
[2]) Journ. chem. Soc. **93** (1908), 1876.

(Δ^6-m-menthenol-8) was formed quantitatively. This possessed an intense odour of peppermint and terpineol, boiled at 106° at 20 mm. pressure and yielded a nitroso-chloride melting at 125°. From the latter, carvestrene dihydrochloride (m. p. 52,5°) and carvestrene dihydrobromide (m. p. 48 to 49°) were obtained by means of hydrohalogen. The cis-tetrahydro carvestrenediol, which was obtained by shaking with dilute sulphuric acid, melted at 94°. By means of magnesium methyl iodide, water could readily be separated from the dihydro isocarvestrenol, and in this process isocarvestrene (b. p. 176 to 177° at 765 mm. press.) together with a diterpene $C_{20}H_{32}$ (di-isocarvestrene) were formed, the latter of which boiled at from 188 to 190° under 20 mm. pressure. It is remarkable that in the case of isocarvestrene it is not only the values of the refraction, but also the fact that the hydrocarbon did not yield the carvestrene derivatives referred to, which point to the presence of conjugated double-linkings in the substance.

Cadinene. In a preliminary note, N. Lepeschkin[1]) reports on case of isomerism in the preparation of cadinene. Cadinene prepared by heating cadinene dihydrochloride (he does not state with what) and possessing the following constants: (b. p. 148 to 149° at 20 mm. pressure; $d\frac{20°}{4°}$ 0,9172; n_D 1,5107; $[\alpha]_D$ — 111,28°) was converted by prolonged heating at 180 to 200° into an isomeric compound (b. p. 145 to 148° at 20 mm. pressure; $d\frac{20°}{4°}$ 0,9061; $n_{D\,20°}$ 1,5041; $[\alpha]_D$ — 2,80°). Isomerism also occurred when the substance was heated with glacial acetic acid. For the preparation of pure cadinene, for which the constants are given as follows: b. p. 271 to 272° at ordinary press.; 149° at 20 mm. press.; $d\frac{20°}{4°}$ 0,9183; $n_{D\,20°}$ 1,5073; $[\alpha]_D$ — 110,96°, the treatment of cadinene dihydrochloride with sodium alcoholate is recommended.

Caryophyllene. By oxidising caryophyllene with permanganate E. Deussen[2]) had previously obtained a body $C_{15}H_{22}O_4$, m. p. 120,5° which is certainly of a glycol like character. Deussen has recently announced[3]) that he has isolated two acids from the products of oxidation. One of these boiled under 16 mm. pressure between 186 and 190, possessed the formula $C_{10}H_{16}O_3$ and proved to be a monobasic ketonic or aldehydic acid, yielding a semicarbazone melting at 186°. The second acid crystallised in coarse square columns, melting at 179,5 to 180,5°. It was a monobasic acid $C_8H_8O_4$, which could not be identified with any known acid. Furthermore, by carrying

[1]) Journ. Russ. phys.-chem. Ges. **40** (1908), 698. Quoted from Chem. Zentralbl. **1908**, II. 1354.

[2]) Liebig's Annalen **359** (1908), 258; Report November **1908**, 178.

[3]) Berl. Berichte **42** (1909), 376, 680.

out the oxidising process in acetone solution with strong cooling, caryophyllene yielded a compound $C_{10}H_{18}O_3$, melting at 146°, which was judged by its behaviour to be a glycol.

Alcohols.

A. Windaus[1]), in a paper on rendering saponin non-toxic by means of cholesterol, states that digitonin may be combined with linalool, geraniol and sabinol into a crystalline compound.

Linalool. By reducing linalool by means of nickel and hydrogen, C. J. Enklaar (as already mentioned in our last Report)[2]) obtained 2, 6-dimethyl octane. We gather from a new paper by Enklaar[3]) that in addition to this hydrocarbon he obtained 2, 6-dimethyl octanol-6 $(CH_3)_2 \cdot CH \cdot (CH_2)_3 \cdot C(OH)(CH_3) \cdot CH_2 \cdot CH_3$ (b. p. 88 to 88,5° at 14 mm. press.; $d\frac{15°}{4°}$ 0,836; $n_{D15°}$ 1,4388) which points to the accuracy of Tiemann's and Semmler's formula for linalool, viz., $(CH_3)_2 : C : CH \cdot CH_2 \cdot CH_2 \cdot C(OH)(CH_3) \cdot CH : CH_2$. By the reaction of magnesium ethyl iodide on 2-methyl heptene-2-one-6 there was formed 2, 6-dimethyl octene-2-ol-6 $(CH_3)_2 \cdot C : CH \cdot CH_2 \cdot CH_2 \cdot C(OH)(CH_3) \cdot CH_2 \cdot CH_3$ (b. p. 94 to 94,5° at 14 mm. press.; $d\frac{15°}{4°}$ 0,8695; $n_{D15°}$ 1,4569) which, when reduced with nickel and hydrogen also yielded 2, 6-dimethyl octane and 2, 6-dimethyl octanol-6.

Menthol. In a preliminary communication, R. H. Pickard and W. O. Littlebury[4]) refer to experiments for the separation of stereoisomeric menthols by the aid of their acid phthalic, or succinic esters. Thymomenthol, a body of a low melting-point, obtained by the reduction of thymol by Sabatier's process, had already been converted by Brunel[5]) by esterification and subsequent hydrolysis into an isomeride, α-thymomenthol. The latter contains three, if not all four of the theoretically possible racemic combinations. Two of these can be characterised accurately and split up into their active component parts. One of these racemic menthols melted at 25°, the acid succinic ester at 86°, and the acid phthalic ester at 131°. From the fractionated crystallisation of the cinchonine or brucine salts of the last-named, a lævorotatory isomeride was obtained which, upon saponification, yielded a menthol with the same melting-point and rotation as the natural

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[1]) Berl. Berichte **42** (1909), 244.
[2]) Report November **1908**, 153.
[3]) Recueil des trav. chim. des P.-B. **27** (1908), 411. Through Chem. Zentralbl. **1908**, II. 1926.
[4]) Proceed. chem. Soc. **24** (1908), 217.
[5]) Compt. rend. **140** (1905), 252; **141** (1905), 1245; Report April **1906**, 117.

combination. The second racemic product had m. p. 48 to 50°. The acid phthalic ester (m. p. 175 to 177°) could be split up into its active component by fractionated crystallisation of the brucine salt.

For the pharmacological behaviour of menthol, see p. 115.

Terpineol. It is some time since Perkin[1]) prepared an inactive terpineol by treating the inactive 1-methyl Δ^1-cyclohexene 4-carboxylic ester with magnesium methyl iodide. An optically active Δ^3-p-menthenol-8 could likewise be obtained by the same method with the aid of inactive 1-methyl Δ^3-cyclohexene 4-carboxylic acid, which by fractional crystallisation of the brucine and strychnine salts could easily be split up into the optically active components[2]). Recently[3]), an easy method has been found for the preparation of the above-named 1-methyl Δ^1-cyclohexene 4-carboxylic acid which also admitted of being readily split up into the two optically active modifications. This method has been used by Perkin, in collaboration with K. Fisher[4]), for the synthesis of the optically active terpineols. When subjected to the action of magnesium methyl iodide, the esters yielded quantitatively the corresponding active terpineols which melted at 35° precisely. The specific optical rotation was found to be $[\alpha]_D$ + 44,2° and — 46,6°, whereas other authors had found higher values for this combination[5]). It was easy to obtain d-$\Delta^{3,8(9)}$-p-menthadiene from the above mentioned d-Δ^3-p-menthenol-8 by the action of magnesium methyl iodide by the cold process, but singularly enough a conversion of the active terpineols into the corresponding limonenes under the same conditions was impossible, because almost complete racemisation supervened. The abstraction of water by means of anhydrous oxalic acid also resulted only in almost pure dipentene.

Terpinenol. In our last Report[6]) we have referred briefly to O. Wallach's synthesis of terpinenol-1, and we now extract the following particulars from the more detailed account of the process which has since appeared[7]).

Δ^3-Isopropyl cyclohexenone (b. p. 95 to 96° at 12 mm. pressure; $d_{22°}$ 0,944; $n_{D22°}$ 1,4817) was treated with magnesium methyl iodide. The resulting alcohol (b. p. 92 to 97° at 14 mm. pressure; $d_{24°}$ 0,9210; $n_{D24°}$ 1,4778; mol. refr. found 47,31, calculated 47,16) boiled at

[1]) Journ. chem. Soc. **85** (1904), 654; Report October **1904**, 97.
[2]) Journ. chem. Soc. **89** (1906), 839; Report October **1906**, 107.
[3]) Journ. chem. Soc. **93** (1908), 1417.
[4]) Ibidem 1871.
[5]) See Report April **1908**, 186.
[6]) Report November **1908**, 180.
[7]) Liebig's Annalen **362** (1908), 279.

ordinary pressure apparently a little below 215°, water being given off. In the course of this reaction, phellandrene was formed, and determined by its odour and by the nitrite-reaction. It follows from this, that a displacement of the double linking must have occurred in some phase or another possibly at as early a stage as in the Grignard reaction. But the fact that the synthetically prepared alcohol contained a high proportion of terpinenol-1 could be proved by oxidation to 1, 3, 4-trihydroxyterpane, m. p. 120 to 121°. This latter substance, when treated with hydrochloric acid, yielded, in addition to cymene, a ketone which was doubtless identical with Δ^1-menthenone. We may further place on record the fact that the optical rotatory power of sabinene hydrate in 19,17% ethereal solution is $[\alpha]_D + 53{,}67°$, while that of synthetic terpinenol-4 is $[\alpha]_D + 10{,}53°$.

Guajol. A. Gandurin[1]), in a preliminary communication, describes experiments relating to the sesquiterpene alcohol guajol. For the purpose of isolating the compound, guajacum-wood oil was shaken up with ether for 12 hours, the resultant pulpy mass filtered with the suction pump, again shaken with ether and recrystallised from alcohol. The guajol ($C_{15}H_{25}OH$) obtained by this process occurs in prismatic crystals; it melted at 91° and, in alcoholic solution, had the rotation $[\alpha]_{D\,25°} - 25{,}64°$. When the substance was rubbed in the dark with a glass-rod, a pronounced irridescence of a blueish colour ensued. A hydroxyl determination according to Tschugaeff-Zerewitinoff showed the alcohol to be monatomic, the determination of the rate of esterification disclosed its tertiary character. Dihydro-guajene ($C_{15}H_{26}$) prepared according to Semmler's process by heating with zinc-dust, showed the following constants: b. p. 122° at 11 mm. press., $d_{4°}^{0°}$ 0,9089, $d_{4°}^{25°}$ 0,8914, $n_{D\,20{,}2°}$ 1,49317, $[\alpha]_{D\,18{,}5°} - 26{,}65°$, molecular refraction determined: 66,99, calculated for a bi-cyclic hydrocarbon $C_{15}H_{26}$/=66,55. As, according to Semmler, secondary alcohols are not attacked by zinc-dust, the formation of dihydro-guajene also points to the tertiary character of guajol. For the ether $C_{15}H_{25}OCH_3$, obtained by the action of methyl iodide upon the potassium compound, the following properties were established: b. p. 141 to 143° at 9 mm. press., $d_{4°}^{0°}$ 0,9513, $d_{4°}^{25°}$ 0,9332, $n_{D\,18{,}5°}$ 1,48963, $[\alpha]_{D\,20°} - 31{,}81°$, mol. refr. found 72,77, calculated for a bi-cyclic ether $C_{15}H_{25}OCH_3$/=72,83. Application on Tschugaeff's xanthogenate method showed that — corresponding to the behaviour of tertiary alcohols — it was impossible to isolate the methyl guajyl-xanthogenate, because it decomposed immediately into guajene. This hydrocarbon showed the follow-

[1]) Berl. Berichte **41** (1908), 4359.

ing constants: b. p. 124° at 11 mm. press., $d_{4^\circ}^{0^\circ}$ 0,9133, $d_{4^\circ}^{25^\circ}$ 0,8954, $n_{D\,25^\circ}$ 1,49468, $[\alpha]_{D\,25^\circ}$ — 66,11°, mol. refr. determined 66,46, calculated for a bi-cyclic hydrocarbon $C_{15}H_{24}$ 66,28. The whole of these results show that guajol is a tertiary sesquiterpene alcohol with one ethylene linking.

Aldehydes.

In the action of organic acids or acid anhydrides upon aldehydes, the formation of di-esters or unsaturated acids is a well-known phenomenon. F. W. Semmler[1]) has now further been able to prove that aldehydes in which a labile hydrogen atom is found in an adjoining position the CHO-group, are more or less easily able to yield mono-esters when subjected to the treatment mentioned above, in which process a conversion of the aldehyde into the enolic form (i. e. into the vinylic form) is to be assumed. Thus, santalol, when oxidised with ozone, yielded saturated tricyclic eksantalal[2]), $C_{11}H_{16}O$, which was now, after being purified by means of the bisulphite combination, found to possess the following constants: b. p. 112 to 113° at 10 mm. press., d_{20° 0,987, n_D 1,4881, α_D about + 12°. This eksantalal, when boiled for an hour with acetic anhydride yielded, in addition to a slight quantity of diacetate, about 80% of enol-eksantalal mono-acetate (dihydro-eksantalol acetate), $C_{10}H_{14}:CH\cdot O\cdot CO\cdot CH_3$. This combination possessed the following properties: b. p. 132 to 135° at 10 mm. press., d_{20° 1,023, n_D 1,4881, α_D — 7° 15′. By heating with water or dilute mineral acids at 110° under pressure, this body could be split up again into the aldehyde. Reduction with sodium in alcoholic solution produced eksantalol $C_{11}H_{18}O$. Whereas even with ozone no carbon atom split off from eksantalal, which indicates the saturated character of the body, the ester yielded a tri-cyclic ketone: nor-eksantalone, $C_{10}H_{14}O$, with the following constants: b. p. 101 to 102° at 10 mm. press., d_{20° 0,988, n_D 1,485, molec. refr. found 43,51, calculated 42,92. Its oxime boiled at 142 to 144° under 10 mm. pressure, and its semicarbazone melted at 216°. The corresponding alcohol, nor-eksantalol, $C_{10}H_{16}O$, boiled (10 mm. pressure) at 116 to 118°.

Phenylacetaldehyde, which behaved entirely analogously, was found to possess the following constants: b. p. 85 to 86° und 10 mm. press., d_{20° 1,0252, n_D 1,53191, molec. refr. found 36,9, calculated for C_8H_8O 36,7. Upon boiling with acetic anhydride it yielded about 80% of enol-phenylacetaldehyde mono-acetate (phenylvinyl acetate, dihydro phenyl ethyl acetate), $C_6H_5\cdot CH:CH\cdot O\cdot CO\cdot CH_3$: b. p. 119 to 121° at 10 mm. press., d_{20° 1,065, n_D 1,5483, molec. refr. found 48,21, calculated for $C_{10}H_{10}O_2$ 46,32. Reduction produced

[1]) Berl. Berichte **42** (1909), 584.
[2]) Compare Report October **1907**, 85; November **1908**, 182.

phenyl ethyl alcohol; oxidation with ozone, benzaldehyde (b. p. 63 to 66° at 10 mm. press.) and benzoic acid (m. p. 121°); it was also possible to split it up into the constituent parts, phenylacetaldehyde and acetic acid. Other aldehydes, such as œnanthic aldehyde, citral, citronellal, etc. showed an analogous behaviour. The well-known formation of isopulegol acetate from citronellal afforded proof that the formation of the enol-acetate precedes the closing of the ring. The physical constants of the aldehydes and their enolic mono-acetates possess regular features which enable the constitution as determined by chemical process to be tested. Moreover, the reactions described above afford a means of breaking up aldehydes into carbonyl combinations possessing one less carbon-atom, and it is further clear that if aldehydes are present when essential oils are acetylated, the alcohol content is certain to be found too high. Semmler's studies also explain certain abnormal reactions of aldehydes, such as the frequently poor yield when aldehydes are prepared from primary alcohols by oxidation with chromic acid in acetic acid solution, and the appearance, during the process of oxidation, of oxidation products containing less carbon. In any case conversions into the vinylic forms also take place on that occasion, and the readiness of aldehydes to polymerise and condense may be traced to the same cause.

A handy process for reducing salicylic acid to salicylic aldehyde is described by H. Weil[1]). When treated with sodium-amalgam at ordinary temperature in the presence of boracic acid, salicylate of sodium yielded the aldehyde, which latter was removed from the action of the reducing agent by simultaneous conversion into a sparingly soluble Schiff's base by means of an aromatic amine. The Schiff's base could then be filtered off and the aldehyde recovered from it by dilute acid.

The same problem is dealt with in a paper by C. Mettler[2]), who succeeded in reducing benzoate and salicylate of sodium to their corresponding aldehydes by electrolysis in the presence of boracic acid, with the aid of a mercury-electrode. In this case the aldehyde was removed from the reaction-mixture by overlaying with benzene.

Piperonal. As stated in our last Report[3]), Delange has substituted for Fittig-Remsen's formula for piperonal dichloride $CCl_2 : O_2 : C_6H_3$, (which had been in general use for several decades,) the formula $CO : O_2C_6H_3 \cdot CHCl_2$. While engaged in experimental control tests of the arguments brought forward by Delange in support of his view, Pauly[4]), who had used the old formula in his investig-

[1]) Berl. Berichte **41** (1908), 4147; German Patent 196239.
[2]) Ibidem 4148.
[3]) Report November **1908**, 194.
[4]) Berl. Berichte **42** (1909), 417.

ations, came to the conclusion that "piperonal dichloride", from piperonal and chloride of sulphur[1]) is, in fact, composed in accordance with the formula expressed by Delange, and not according to the old formula, which had also been adopted by us at the time. Pauly was able to afford direct proof that when reducing "piperonal dichloride" made in accordance with the patent above referred to, and purified by him by a special process, with zinc-dust in glacial acetic acid solution at a temperature not exceeding 55 to 60°, he did not recover piperonal, but instead there of the cyclic carbonic acid ester (m. p. 34°) of methyl pyrocatechol, $CO:O_2:C_6H_3\cdot CH_3$, from which, by saponification with a 50 per cent. pyridin solution, free methyl pyrocatechol, $(HO)_2\cdot C_6H_3\cdot CH_3$, was obtained. This possessed a melting point of 65°, whereas up to the present 51° has been stated. The only inference to be drawn from this result is that in the course of the action of sulphur chloride on piperonal there is formed primarily a piperonal dichloride of the old formula, but that, possibly, this body, under the formation of sulphurous intermediary compounds, is converted into the cyclical carbonate of methyl pyrocatechol dichlorinated in the side-chain. According to Pauly, the circumstance that when piperonal dichloride obtained in this manner is worked up, larger or smaller quantities of protocatechuic aldehyde carbonate are produced, affords confirmation of his theory.

In connection with Pauly's communication, Barger[2]), points out that very soon after the publication of Delange's paper, he ranged himself on the side of that investigator[3]) in consequence of the results obtained when acting with thionyl chloride upon combinations with the methylenedioxy-group. Barger was able to show that with thionyl chloride, piperonal at a relatively low temperature yields piperonal dichloride, from which piperonal could be regenerated with formic acid. At 180°, however, the CH_2O_2-group was also attacked, resulting in the formation of "piperonal dichloride", $CO:O_2:C_6H_3\cdot CHCl_2$, while the excess of thionyl chloride was reduced to chloride of sulphur.

Homopiperonal. To the already known reactions for distinguishing propenyl from allyl compounds, such as the different behaviour of these compounds towards acetate of mercury[4]) or towards concentrated formic acid[5]), F. W. Semmler and K. Bartelt[6]) have added a new one. This process deals with the action of ozone

[1]) German Patent 165727 of Schimmel & Co.
[2]) Berl. Berichte **42** (1909), 763.
[3]) Journ. chem. Soc. **93** (1908), 563, 735.
[4]) Berl. Berichte **35** (1902), 2995; **36** (1903), 3575; Report April **1903**, 83; April **1904**, 100; April **1906**, 100.
[5]) Berl. Ber. **41** (1908), 2185; Report November **1908**, 51.
[6]) Berl. Ber. **41** (1908), 2751.

upon the combinations in question. By splitting-up with water the ozonides which are formed it is found that the propenyl compounds yield the corresponding aldehydes (isosafrol, for instance, yielding piperonal), whereas allyl compounds give the corresponding homologous combinations. For example: safrol yielded, besides homopiperonylic acid, a considerable proportion of homopiperonal possessing the following properties: m. p. 69°, b. p. 143 to 144° under 10 mm. pressure, $d_{20°}$ 1,295, n_D 1,57117, mol. refr. found 41,67, calculated 41,69. The semicarbazone melted at 189°, the oxime (b. p. 180 to 181° at 10 mm. pressure; m. p. 124 to 125°) yielded upon boiling with acetic anhydride homopiperonylic acid nitrile (b. p. 153 to 156° at 10 mm. pressure; $d_{20°}$ 1,231; n_D 1,53698) from which by saponification homopiperonylic acid, $C_9H_8O_4$ (m. p. 127°), was obtained. The methyl ester (b. p. 153 to 155° at 10 mm. pressure; $d_{20°}$ 1,246; n_D 1,534; mol. refr. 47,73, calculated 47,98) when reduced with sodium in alcoholic solution, yielded homopiperonyl alcohol $C_9H_{10}O_3$ (b. p. 156° at 10 mm. press. n_D 1,54780) with an odour reminding of ylang-ylang. When the nitrile referred to above was reduced, a base $C_9H_{11}O_2N$ (b. p. 146 to 148° at 10 mm. press; $d_{20°}$ 1,225; n_D 1,5620) was formed of which the picrate melted at 160°.

Lævulic aldehyde. Lævulic aldehyde obtained by action of ozone upon unsaturated compounds such as allylacetone, methyl heptenone, 2,6-dimethyl heptadiene-2,5, citral, geraniol, linalool, caoutchouc, and gutta percha has been more closely examined by C. Harries and M. Boegemann[1]). We will only briefly mention here that a series of experiments pointed to the probability of the compound possessing the formula $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHO$, but in a few cases it behaved abnormally, which was probably due to steric conditions.

Ketones.

Sabina ketone. In continuation of previous syntheses carried out by means of sabina ketone, O. Wallach[2]) has now prepared some symmetrical di-isopropyl derivatives. He condensed sabina ketone with isopropyl magnesium iodide, and by decomposing the resulting product, he obtained an alcohol with an odour reminding of terpineol, and a b. p. of 102 to 107° at 14 mm. pressure. When shaken with dilute sulphuric acid this alcohol was slowly converted into the corresponding terpine:

[1]) Berl. Berichte **42** (1909), 439.
[2]) Liebig's Annalen **362** (1908), 283.

m. p. 139°. By treating it with hydrohalogen he also succeeded in preparing the di-hydrochloride (m. p. 111 to 112°) and the di-hydrobromide (m. p. 120 to 121°).

Menthone. We desire to give some further particulars of a paper by O. Wallach[1]) to which reference has already been made in our last Report[2]). A synthesis of i-menthone was carried out in the following manner. By condensing 1, 4-methyl cyclohexanone with bromo-isobutyric ester and further treating the product by the method frequently described, a hydrocarbon $CH_3 - \langle\rangle = C = C(CH_3)_2$ was prepared and inverted into i-menthene[3]). The i-menthenone obtained therefrom by means of its nitroso-chloride was then reduced to i-menthol and from this i-menthone was obtained by oxidation. The semicarbazone of this compound melted at 210 to 212°, the oxime at 77 to 79°. Hereby its identity with i-menthone obtained from 1, 3, 4-trihydroxy-terpane in the sequence of reactions already described, was demonstrated.

Further, by brominating Δ^4-menthenone, a dibromide (m. p. 36°) was obtained, while reduction yielded a not entirely congealing menthol which obviously contained a mixture of stereoisomeric menthols. The presence of i-menthol could be proved by oxidising the substance to a ketone, from the semicarbazone of which portions of 210 to 212° m. p. could be isolated. Up to the present nothing has yet been determined as to the nature of those fractions of the semicarbazone which have a lower melting point.

E. Beckmann[4]), has continued, in collaboration with E. Müller his researches into the optically active menthones, to which we briefly referred at the time[5]). It is known that l-menthone, $[\alpha]_D$ — 28,5°, which had been previously obtained from natural l-menthol by oxidation with chromic acid mixture, could be converted with cold 90% sulphuric acid into a dextrorotatory isomer, $[\alpha]_D$ + 28,1°. The original surmise that notwithstanding the equal degree of rotation, this case was not one of a simple optical antipode of the original ketone, was confirmed in the sequel by the isolation of a strongly dextrorotatory ketone, d-isomenthone, from the mixture with unaltered l-menthone. From a mixture of several isomeric mentholes which occur in the process of reducing l-menthone or inverted d-menthone, a d-isomenthol (m. p. 78 to 81°; $[\alpha]_D$ + 2,03°) was also obtainable and from this, again, d-isomenthone, $[\alpha]_D$ up to + 35,1°. Reduction of the oximes

[1]) Liebig's Annalen **362** (1908), 261.
[2]) Report November **1908**, 180.
[3]) Report October **1906**, 114.
[4]) Berl. Berichte **42** (1909), 846.
[5]) Report April **1904**, 116.

of the separate menthones into the menthylamines, and the conversion of the latter by means of nitrous acid, resulted in derivatives of still higher rotating-power; thus, from the lævorotatory total product there was obtained a d-isomenthol, $[\alpha]_D + 25{,}6°$, and, further, from such a body with $[\alpha]_D + 26{,}3°$, m. p. 83°. there was prepared an isomenthone with the high specific rotation $[\alpha]_D + 93{,}2°$.

That inverted d-menthone is made up of several isomers has also been shown recently by the investigation of the oximes. Whereas '-menthone oxime melts at 59°, the oxime of inverted d-menthone appears as a viscous oil, which, however, like the oxime of the former, yields a crystalline hydrochlorate. The solid hydrochloride, which was seperated out from a solution of inverted d-menthone in absolute ether by the introduction of relatively little dry hydrogen chloride, possessed when purified, a melting point of 132°, (it turned brown), and a sp. rot. $[\alpha]_D + 35{,}9°$. Hydrochloric acid being again introduced into the filtrate of these crystals, there separated out another hydrochloride, at first of a viscous consistency, but solidifying when dried *in vacuo* over soda-lime. This hydrochloride had $[\alpha]_D - 62{,}6°$, and melted at 117 to 118° (turning brown in the process). It corresponds to the oxime-hydrochloride of true l-menthone, while the hydrochloride which was first separated is identical with the corresponding derivative of d-isomenthone.

The oximes which were liberated from the hydrochlorides by means of sodium carbonate possessed the following characteristics: the viscous oxime of inverted d-menthone had $[\alpha]_D - 6°$; the oxime of l-menthone melted at 59°, and had $[\alpha]_D - 42{,}5°$; the oxime of d-isomenthone was again viscous and had $[\alpha]_D + 41{,}0°$. The pure ketones forming the bases of the oximes could not be recovered unaltered from the latter, on account of the inversion which ensued during the splitting-up process, but after the foregoing there was no doubt that inverted d-menthone consists of a mixture of l-menthone and d-isomenthone.

Experiments previously made to separate the ketones over the semicarbazones were repeated and then led to the following results: inverted d-menthone yielded a semicarbazone, m. p. 116°, and with a specific rotation, in aqueous solution of chloral hydrate, $[\alpha]_D + 26{,}6°$, the semicarbazone from d-isomenthone had a melting point of 154° and $[\alpha]_D + 46{,}5°$, and the derivative of l-menthone, m. p. 184, which had already been prepared before, had a specific rotation of — 64°.

Pulegomenthone which was previously obtained from pulegone hydrobromide could not be split up by similar treatment of its oxime with hydrochloric acid.

Beckmann finally announces that he intends to publish elsewhere a detailed report on this and allied investigations.

Camphor. Further detailed particulars concerning the total synthesis of racemic camphor, which was first carried out by G. Komppa several years ago are now available[1]). Long ago the researches of Haller[2]), and of Bredt and v. Rosenberg[3]), had described a process for the conversion of active camphoric acid into active camphor, but the problem still remained of converting Komppa's synthetic racemic camphoric acid[4]), by this process, into camphor. For this purpose the acid (m. p. 202 to 203°; $\alpha_D \pm 0°$) was converted into campholide by the reduction of its anhydride (m. p. 220 to 220,5°). This campholide melted at 211,5 to 212° and yielded bromocampholic acid (m. p. 178 to 179°). The cyanocampholic acid obtained by heating of campholide with potassium cyanide was saponified to the corresponding homocamphoric acid (m. p. 231 to 232°), the calcium salt of which, when subjected to dry distillation, was converted into racemic camphor with a m. p. of 178 to 178,5°, this melting point not being reduced when the substance was mixed with a preparation obtained by combination of d- and l-camphor. The oxime melted at 118°. Komppa has also projected a total synthesis of active camphor by the splitting-up of racemic camphoric acid into its active components by the aid of quinine, (by which process it has already been possible to produce pure l-camphoric acid,) or by splitting-up camphor itself over the corresponding borneols.

Induced by this communication, E. Beckmann[5]), has published the result of experiments which were made by him, jointly with E. Saran, as far back as in 1897. Isoborneol prepared by us from camphene by Bertram's and Walbaum's process, only possessed a rotation of a few degrees and consisted chiefly of a racemic mixture, for the derivatives obtained from it (camphor m. p. 177°, camphoric acid m. p. 200 to 202°, camphoric anhydride m. p. 219 to 220°,) also rotated but very feebly. For separation into the optically active component parts, the acid cinchonidine salt of camphoric acid, melting at 196 to 198°, was employed. By fractionated crystallisation, dextro and lævorotatory camphoric acid, (m. p. 183°; $[\alpha]_D + 44{,}4°$; and m. p. 186 to 187°, $[\alpha]_D - 50{,}7°$ respectively) were obtained from this. Besides the above, experiments were tried of separating the isoborneol itself by fractional crystallisation of the cinchonidine salt (m. p. 107°) of its acid succinate, but this process of decomposition was only partly carried out. Afterwards, Pickard and Littlebury succeeded in completely decomposing isoborneol by an analogous process, with regard to which we made a communication at the time[6]).

[1]) Berl. Berichte **41** (1908), 4470.
[2]) Compt. rend. **122** (1896), 446; **130** (1900), 376.
[3]) Liebig's Annalen **289** (1896), 1.
[4]) Berl. Berichte **36** (1903), 4332; Report April **1904**, 98.
[5]) Berl. Berichte **42** (1909), 485.
[6]) Comp. Report April **1908**, 185.

Isopulegone. The treatment of isopulegone with magnesium methyl iodide and the conversion of the resulting 3-methyl isopulegol into 3-methyl $\Delta^{2,8(9)}$-menthadiene, to which reference has already been made in our last Report[1]), has been the subject of a detailed paper by A. Ebert[2]). For particulars as to constants, as well as for details concerning the mode of the splitting-off of water (which was carried out according to various methods), we refer to the original paper.

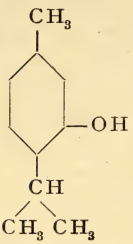
Umbellulone. F. W. Semmler[3]) has recently entered the lists once more in the controversy which is being carried on between Tutin and himself on the constitution of umbellulone; his object on this occasion being to controvert Tutin's objections, which were discussed in our recent Reports[4]). Tutin having maintained that Semmler's arguments referred in reality to a foreign body which was mixed with the umbellulone, the latter repeated his experiments, using for that purpose an umbellulone which had been regenerated from the semicarbazide compound. Umbellulone, obtained by fractionating an oil distilled by us, was found to possess the following constants: b. p. 92 to 94° at 10 mm. press., $d_{20°}$ 0,950, n_D 1,4872, α_D — 37° 30′. In addition to the semicarbazide-semicarbazone which had already been described by another investigator (and which Semmler now showed to possess a m. p. above 200°), the author was also able to prepare the normal mono-semicarbazone with a m. p. between 240 and 243°. The umbellulone regenerated from the last-named product by decomposition with dilute sulphuric acid gave the following constants: b. p. 92,5 to 93° at 10 mm. press., $d_{20°}$ 0,950, n_D 1,48325, α_D — 36° 30′. The preparation obtained from the semicarbazide-semicarbazone showed the following constants: b. p. 92 to 94° at 10 mm. press., n_D 1,4825, α_D — 37°. For β-dihydro umbellulol obtained from the regenerated umbellulone the following constants were determined: b. p. 88 to 92° at 10 mm. press., $d_{20°}$ 0,927, n_D 1,4696, α_D — 27° 45′; for β-dihydro-umbellulone: b. p. 84 to 86° at 10 mm. press., $d_{20°}$ 0,925, n_D 1,4616, α_D — 30°. The benzylidene-compound prepared from the last-named, when oxidised with permanganate in acetone solution, yielded (as before) homotanacetone dicarboxylic acid (m. p. 147°). Hence the assertion of Tutin, that Semmler's benzylidene compound was not derived from β-dihydro-umbellulone, falls to the ground. Without doubt the quantitative conversion into thymol (m. p. 52°, b. p. 111° at 10 mm. press., $d_{20°}$ 0,977, n_D 1,52148, α_D ± 0°) by prolonged heating

[1]) Report November **1908**, 186.
[2]) Zeitschr. d. allg. oesterr. Apoth. Ver. **46** (1908), 545, 561, 573, 589.
[3]) Berl. Berichte **41** (1908), 3988.
[4]) Report April **1908**, 108; November **1908**, 126.

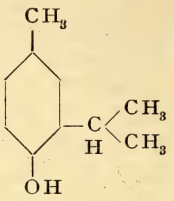
of umbellulone in a sealed tube, which has now been carried out by Semmler, is evidence of the correctness of that investigator's statement as to the constitution of umbellulone.

Phenols and Phenol-Ethers.

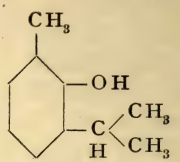
In his dissertation[1]), of which a copy was courteously sent to us, C. Guillaumin describes ortho and parathymol.



m-Thymol (ordinary)



p-Thymol



o-Thymol

For the preparation of para-thymol, para-thymol methyl ether (prepared from pseudo-allylcresol methyl ether and sodium in alcoholic solution), was treated in acetic acid solution according to Störmer's method with hydrobromic acid. Ortho-thymol is prepared in precisely the same manner.

Para-thymol occurs in long, colourless needles, m. p, 36°, b. p. 228 to 229° (corr., at 760 mm. press.), $d_{0°}$ 0,9954, $d_{17,8°}$ 0,9817, $^{n}D_{17,8°}$ 1,52438. The odour of para-thymol is less pronounced than that of ordinary thymol, and reminds of para-cresol.

Ortho-thymol was not obtained in crystalline form; it appears as a colourless liquid, b. p. 225 to 226° (corr., at 760 mm. press.), $d_{0°}$ 0,9986, $d_{15,2°}$ 0,9865, $^{n}D_{15,2°}$ 1,52385.

After giving a list of the literature existing on the pharmacological behaviour of thymol, the author compares this behaviour with that of the new isomers.

With regard to toxicity, experiments on rabbits gave the following results: —

The fatal dose per kilo rabbit was: —

0,033 g. for ordinary thymol;
0,036 g. for p-thymol;
0,045 g. for o-thymol.

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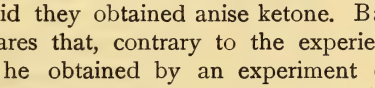
[1]) C. Guillaumin, Étude chimique et pharmacologique des thymols synthétiques dérivés des acides crésotiniques. Paris 1909.

As regards antiseptic action, para-thymol does not appear to be inferior to the natural product, but ortho-thymol is only half as effective.

In order to form an opinion as to the possibility of employing thymol as a remedy for intestinal worms, the author has experimented with such worms (anchylostomum), but here also he found ordinary thymol to be superior to its isomers, while ortho-thymol had the least powerful effect.

In respect to therapeutic efficiency the natural product appears from this to be superior to both isomers.

L. Balbiano[1]), by treating anethol with acetate of mercury, had prepared two glycols of anethol from which, by dehydration, he obtained a hydrocinnamic aldehyde. On the other hand, Tiffeneau and Daufresne[2]) alleged that by treating one of the glycols with 20 % sulphuric acid they obtained anise ketone. Balbiano now, in a fresh paper[3]), declares that, contrary to the experience of Tiffeneau and Daufresne, he obtained by an experiment carried out in the same way, from both glycols (the α-glycol, m. p. 62 to 63° and the β-glycol, m. p. 114 to 115°) the same p-methoxy hydrocinnamic aldehyde (b. p. 136 to 137° at 10 mm. press.; semicarbazone, m. p. 175 to 176°). In addition there was formed a small quantity of a compound (m. p. 181 to 182°) to which, from its behaviour, the followiug formula is assigned: —



For details, we refer to the original paper.

With regard to the occurrence of 1-allyl-2, 3, 4, 5-tetramethoxybenzene in French oil of parsley, see p. 73.

Acids.

The ketone $C_7H_{10}O$[4]) which was obtained by Wallach by the oxidation of Δ^1-cyclohexene acetic acid or Δ^1-methylcyclohexene and which, upon further oxidation, yielded glutaric acid, the nature of which,

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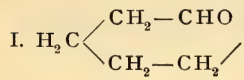
[1]) Comp. Report April **1906**, 99.

[2]) Compt. rend. **144** (1907), 1354; Report October **1907**, 169.

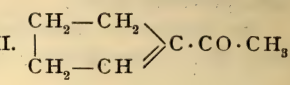
[3]) Rendiconti della R. Acc. dei Lincei **17** (1908), 259. We quote from a copy kindly sent to us.

[4]) Liebig's Annalen **343** (1905), 53; **353** (1907), 292; **359** (1908), 308 Report April **1906**, 128; October **1907**, 177; November **1908**, 197.

however, had to be determined still, has now been recognized as Δ^1-acetylcycl opentene. This statement has been made in a joint paper by O. Wallach and W. H. Perkin jun.[1]). Perkin, when oxidising the ethyl ester of the Δ^1-cyclohexene acetic acid with ozone[2]), had obtained an aldehydo ketonic ester (I) which, when boiled with sulphuric acid, was converted into Δ^1-acetyl cyclopentene (II) which could be identified with the ketone $C_7H_{10}O$ obtained from the acid itself.



I.



II.

By condensing cyclopentanone with bromo-propionic ester according to the series of reactions generally used for the preparation of tetrahydrated extracyclic ring ketones[3]), Wallach had also succeeded in producing Δ^1-acetyl cyclopentene and had also recognized its identity with the ketone obtained from cyclohexene acetic acid, because the derivatives of the two ketones possessed the same properties (oxime m. p. 90 to 91°, benzoyl oxime m. p. 116 to 117°; semicarbazone m. p. 203 to 204°). According to Perkin's experiments it is to be assumed that Δ^1-cyclohexene acetic acid produces in the first place a ketonic aldehyde which is immediately converted, by internal condensation, into acetyl cyclopentene. Such an unlooked-for result of an oxidation with permanganate shows the extreme caution which must be exercised in forming theories regarding the constitution of a body from oxidative analysis.

Cinnamic acid. With regard to the complicated isomerism of the different cinnamic acids, new and far-reaching researches have been published, the main features of which we will briefly pass in review.

E. Erlenmeyer jun.[4]) has made investigations into the problem as to what is the origin of the difference between synthetic cinnamic acid and natural cinnamic acid from storax. The two acids differ, for instance, in the manner in which they crystallise from ether, as well as in regard to solubility. The synthetic acid melts at 132 to 133°, the acid from storax at 134 to 135°. It was shown that synthetic cinnamic acid is a uniformly crystallising mixture made up of about equal parts of storax-α-acid and an isomeric combination termed hetero-α-cinnamic acid. It is very difficult to split up the mixture by crystallisation, as the two component parts evidently exert mutual molecular attraction. No admixture of other products could be detected.

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[1]) Berl. Berichte **42** (1909), 145.
[2]) Journ. chem. Soc. **93** (1908), 1946.
[3]) Report November **1908**, 166.
[4]) Berl. Berichte **42** (1909), 502.

In order to separate the synthetic cinnamic acid into its component parts, the ethyl ester was subjected to careful fractional distillation *in vacuo*. After saponification there was obtained, from the fractions with the lowest boiling points, storax cinnamic acid, and from those with the highest boiling points and from the residue the combination formerly [1]) described as "new triclinic cinnamic acid", and now as "hetero-cinnamic acid". This combination, like the storax acid, can occur either in the α or the β-form, and the two forms can be both converted into each other. The acid recovered from the residue by the method of separation above indicated was the β-form. It occurred as a lustreless, light, chalky powder; m. p. 128°. It was more readily soluble in water, ether, alcohol, or ligroin than were either the storax acid or the synthetic acid. The acid was easily convertible into the α-form, which separated out in lustrous, small crystalline flakes, but the hetero-β-cinnamic acid was less inclined to conversion than was the storax-β-acid, and it was therefore generally very easy to re-convert the hetero-α-cinnamic acid into the β-acid. The m. p. of the hetero-α-acid was 130 to 131°. In the method of separation by the aid of the esters, as set forth above, the β-acid was formed from the α-acid by conversion, because the synthetic cinnamic acid was obtainable in its characteristic crystalline form by combination of hetero-α-cinnamic acid and storax-α-cinnamic acid after crystallisation from ether, whereby the proof of its composition was given. The two acids formed mixed crystals in every proportion; but on the other hand, when hetero-β-cinnamic acid and storax-α-acid were dissolved together, the former was partly converted into hetero-α-acid, so that crystallisations of altogether different characteristics were obtainable. No uniform mixed crystals were observed in this case.

A further paper [2]), connecting with that abstracted above, discusses the differences in chemical behaviour of the isomeric acids obtained from synthetic cinnamic acid as regards the formation of salts and the additive reactions. Without entering into details, we will only mention, that besides salts which showed great exterior resemblance, others were obtained which presented marked differences. In the matter of additive reactions, the two acids distinguished themselves by considerable divergence in the rate of speed of the reactions. By means of fractionated precipitation of the sodium salt with hydrochloric acid it was furthermore possible, owing to the difference in strength of the two acids, to devise a process for splitting-up the synthetic acid into its two component parts. Worthy of note also is the property possessed by storax acid, synthetic cinnamic acid and hetero-β-acid, as monobasic acids, of yielding acid salts which must be derived from double

[1]) Report April **1907**, 156.
[2]) Berl. Berichte **42** (1909), 182.

molecules. But as regards this property, analogous behaviour has been observed in other cases, for instance in that of benzoic acid. In fact, the ability of giving double molecular reactions appears to be more frequent generally than could have been expected up to the present. Erlenmeyer attributes the isomerism observed in the cinnamic acids to the power possessed by the benzene nucleus of existing in several more or less stable conditions which, in the case of the cinnamic acids, are distinguished by special stability. Thus it was possible to obtain the benzaldehydes corresponding to the two cinnamic acids; but particulars as to this part of the investigations are deferred to a subsequent communication.

Shortly before the appearance of the above-mentioned work of Erlenmeyer, a paper by E. Biilmann[1]) had appeared, which seemed to give a surprisingly simple solution of the problems of isomerism which exist in the chemistry of cinnamic acids. In this paper no speculations with regard to new varieties of isomerism were propounded. In Biilmann's opinion, allo-cinnamic acid (m. p. 68°) and the two iso-cinnamic acids with respective melting points of about 57° and 38 to 46°, are not isomeric, but are chemically identical bodies, in which the only question at issue is one of simple trimorphy. Provided certain exceptional measures of precaution were observed, each of the three acids could be converted quantitatively in the time of a few seconds into any of the others, by melting it and inoculating the molten substance, when cooled, with the desired variety. Thus a plausible explanation might be found for the origination of the separate forms. But Erlenmeyer[2]) points out that Biilmann's observations are not quite sufficient to disprove the theory that the three cinnamic acids present exceedingly labile, mutually inter-convertible isomers. The assumption of simple polymorphy would not be consonant with several of the facts observed, and further investigations are therefore considered necessary before a definite opinion can be formed.

Nitrogenous Bodies.

From a paper by F. Weehuizen[3]) we abstract the following data, referring to the detection of indol in flowers. If the available quantity of flowers is large enough to admit of the preparation of essential oil, the presence of indol may be proved by means of the crystalline combinations which it gives with sodium bisulphite and picric acid. In other cases the method given by Verschaffelt[4]) may be applied,

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[1]) Ibidem 513.
[2]) Ibidem 521.
[3]) Pharm. Weekblad **45** (1908), 1325. From a copy kindly sent to us.
[4]) Report October **1905**, 123

in which the odour exhaled by the flowers is allowed to act upon oxalic acid. Weehuizen has now successfully tested the practicability of the colour reactions for indol indicated by Steensma[1]) for showing the presence of this combination in the scent of flowers. The crushed flowers were extracted with alcohol for about 5 minutes, and a little vanillin or p-dimethylamino benzaldehyde was dissolved into the filtrate, whereupon after the addition of a few drops of concentrated hydrochloric acid the characteristic red colorations ensued. When p-dimethylamino benzaldehyde was employed, the reaction could be made still plainer by the addition of a trace of sodium nitrite. As phloroglucinol gives the same colour reactions, another process, which may be followed when this combination is present, is that of exposing filtering paper or spun glass soaked in a 1 % solution of vanillin or p-dimethylamino benzaldehyde in a mixture of equal volumes of alcohol and concentrated hydrochloric acid, for a long time to the exhalations of the flowers. When dried at ordinary temperature ared coloration will then take place. The last-named process is also to be applied when the alcoholic extracts of the flowers are coloured.

In this manner the presence of indol could be shown in the white flowers of *Murraya exotica* L. *(Murraya sumatrana* Roxb.) and in the spadices of one of the numerous varieties of *Caladium* with variegated leaves.

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[1]) Zeitschr. f. physiol. Chem. **47** (1906), 25.

Solubility Table of the Most Used Odoriferous Substances.

100 parts by weight of solvent dissolve at 10° C.	96 p. c. Alcohol	70 p. c. Alcohol	Glycerine	Olive oil	Paraffin oil
Anethol	20	3	s. l.[1])	10	6
Anisic aldehyde (Aubépine)	∞[2])	130	0,1	∞	1,5 (opal.)
Benzaldehyde	∞	70	0,1	∞	7
Benzoic acid ethyl ester .	∞	45	s. l.	∞	∞
Benzoic acid methyl ester	∞	65	0,1	∞	∞
Benzyl acetate	∞	50	0,1	∞	13
Benzyl alcohol	∞	∞	∞	∞	1
Benzyl benzoate . . .	∞	3	s. l.	∞	18
Bornyl acetate	∞	30	s. l.	∞	∞
Cassia oil, artificial, Sch. & Co. (see cinnamic aldehyde).					
Cinnamic aldehyde. . .	∞	30	0,1	∞	1,5 (opal.)
Cinnamic alcohol . . .	∞	∞	1	11	0,7
Cinnamic acid benzyl ester	∞	1,5 (cloudy)	s. l.	∞	4 (opal.)
Cinnamic acid ethyl ester	∞	13	s. l.	∞	∞
Cinnamic acid methyl ester	∞	50	s. l.	∞	∞
Cinnameïn (see Peru balsam oil).					
Citral	∞	40	s. l.	∞	∞
Citronellal.	∞	25	s. l.	∞	∞ (opal.)
Citronellol.	∞	55	0,1	∞	∞
Coumarin[3])	8	4	0,1	1,5	0,3
Eucalyptol	∞	55	0,1	∞	∞
Eugenol	∞	110	0,1	∞	3 (opal.)
Geraniol	∞	65	0,1	∞	∞
Geranyl acetate	∞	6 (cloudy)	s. l.	∞	∞

[1]) s. l. = solubility less than 0,1 : 100.
[2]) ∞ = soluble in any proportion.
[3]) For details as to the solubility of coumarin in alcohol, see Report April 1899, 66.

100 parts by weight of solvent dissolve at 10° C.	96 p. c. Alcohol	70 p. c. Alcohol	Glycerine	Olive oil	Paraffin oil
Geranyl methyl ether . .	∞	6 (opal.)	s. l.	∞	∞
Heliotropin (Piperonal) .	8	5	s. l.	6	0,8 (opal.)
Hyacinth, Sch. & Co. . .	∞ (opal.)	3 (opal.)	s. l.	∞	2 (opal.)
Isoeugenol	∞	115	0,1	∞	0,7 (opal.)
Isosafrol	∞	2	s. l.	∞	∞
Jasmine, Sch. & Co. . .	∞	150	0,1	∞	2
Lilac, Sch. & Co. . . .	∞	65	0,1	∞	∞
Lily of the Valley, Sch. & Co.	∞	100	0,1	∞	4
Linalool	∞	50	0,1	∞	∞
Linalyl acetate (Bergamiol)	∞	24	0,1	∞	∞
Menthol	300	23	0,1	10	10
Methylanthranilic acid methyl ester	∞	7	s. l.	∞	∞
Musk, artificial, Sch. & Co.[1])	0,5	s. l.	s. l.	2,5	0,7
Musk, artificial, Sch. & Co., extra soluble	1,1	0,2	s. l.	2,5	0,7
Musk-seed (Ambrette) oil, Sch. & Co.	∞	2	s. l.	∞	∞
Muguet (see Lily of the Valley).					
Narcissus, Sch. & Co. . .	∞	95	0,1	∞	∞
Neoviolone 100% . . .	∞	40	s. l.	∞	∞
Neroli, Sch. & Co. . . .	∞	35	s. l.	∞	∞
Nerolin I	5	0,8	s. l.	13	6
Nerolin II	2	0,4	s. l.	3	2
Niobe oil (see Benzoic acid methyl ester).					
Novoviol	∞	25	s. l.	∞	∞
Orris oil, liquid, Sch. & Co.	∞	6	s. l.	∞	∞
Orris oil, solid	10	s. l.	s. l.	2	0,8
Paracresol methyl ether .	∞	10	0,1	∞	∞
Peru balsam oil	∞	1,5 (opal.)	s. l.	∞ (opal.)	0,7 (opal.)
Phenyl ethyl alcohol . .	∞	∞	1,5	∞	1,5

[1]) For solvents for artificial musk, see also Bericht April **1905**, 123.

100 parts by weight of solvent dissolve at 10° C.	96 p. c. Alcohol	70 p. c. Alcohol	Glycerine	Olive oil	Paraffin oil
Pink blossom oil, Sch. & Co.	∞	80	0,1	∞	1,5 (opal.)
Reseda-Geraniol, Sch. & Co.	∞	50	0,1	∞	∞ (opal.)
Rose oil, artificial, Sch. & Co.	20[1])	20[1])	s. l.	50	50
Rose oil, artificial, liquid, Sch. & Co.	∞	30[2])	s. l.	∞	∞
Rose oil, natural, free from stearoptene	∞	30	s. l.	∞	∞
Safrol	∞	3	s. l.	∞	∞
Salicylic acid amyl ester	∞	1	s. l.	∞	∞
Salicylic acid ethyl ester	∞	7	s. l.	∞	∞
Salicylic acid methyl ester	∞	11	0,1	∞	∞
Santalol	∞	25	0,1	∞	∞
Terpineol, liquid	∞	60	0,1	∞	∞
Thymene	∞	1	s. l.	∞	∞
Thymol	200	30	0,1	50	5
Tréfol (see Salicylic acid amyl ester).					
Vanillin	38	30	1	0,9	s. l.
Wallflower, Sch. & Co.	∞	∞	0,1	∞	0,4 (opal.)
Wintergreen oil, artificial (see Salicylic acid methyl ester).					
Ylang-Ylang, Sch. & Co.	∞	40	s. l.	∞	∞

[1]) Soluble with strong separation of paraffin; completely soluble only when greatly diluted.
[2]) Soluble with slight separation of paraffin; completely soluble only when greatly diluted.

Examination of the Essential Oil

of

Blumea balsamifera D. C.

By

Richard Jonas

of Brussels.

Blumea balsamifera, a shrub-like plant of the family of the *Compositæ*, is a native of India, and occurs from the Himalayas down to Singapore and the Malay Archipelago. According to recent reports it also flourishes abundantly in Tonquin[1]). The product of distillation of the plant is solid and consists of the so-called "Ngai-camphor", with which only very little liquid oil is found admixed. This Ngai-camphor (*Ngai-fên*) is used by the natives of the countries aforenamed for medicinal purposes and in religious rites, as well as in the preparation of Indian ink. It was first recognized as l-borneol by Plowman[2]), Flückiger[3]), and Haller[4]). With this exception nothing was known up to the present as to the chemical composition of true Ngai-camphor oil. A number of years ago, Schimmel & Co. came into possession of a dark-brown oil, possessing a characteristic odour reminding of borneol, but probably this oil had already been freed from the bulk of its borneol by distillation with water vapour.

This oil possessed the following properties: $d_{15°}$ 0,950, α_D — 12° 30′, $n_{D\,20°}$ 1,48151, acid no. 23,35, ester no. 1, ester no. after acetylation 198 (corresponding to 63,95 % of alcohol $C_{10}H_{18}O$). Fractional distillation under reduced pressure yielded a first fraction of 6,3 g. of an oil with b. p. 38° (40 mm. press.) to 80° (30 mm. press.). In this, as well as in the next fraction, cineol could be identified by the iodol compound m. p. 111,5°. The next following fraction (α_D + 4° 10′) which distilled between 80° (30 mm. press.) and 75° (12 mm. press.) gave a nitroso chloride with a m. p. of 103,5°. Taking into account the boiling point of this fraction it is probable that the nitrosochloride was that of limonene. As the further progress of distillation *in vacuo* was made difficult through the liberal separation of solid crystals (borneol) it became necessary to remove this substance by freezing it out. But before this was done the oil was first treated with dilute sodium carbonate solution and subsequently with a 5 % soda liquor. With the latter, a phenol-like body was isolated from the oil, to which detailed reference shill be made below. The sodium carbonate solution dissolved traces of two solid acids, probably palmitic acid and myristic acid. The crystals which separated under strong cooling from the phenol-and-acid-free oil consisted of a mixture of l-borneol and l-camphor. In order to isolate the borneol, part of this mixture

[1]) Journ. d'Agriculture tropicale **8** (1908), 30; Report April **1908**, 150.
[2]) Pharmaceutical Journal III. **4** (1874), 710; Neues Repert. f. d. Pharm. **23** (1874), 325.
[3]) Pharmaceutical Journal III. **4** (1874), 829.
[4]) Bericht October **1889**, 54.

was heated for 6 hours to 110° with phthalic anhydride in an autoclave; the resulting acid phthalic ester dissolved in dilute sodium carbonate solution, and the alkaline solution after having been repeatedly extracted with ether, distilled in a steam current with addition of soda liquor. The borneol, which volatilised readily with water vapour, congealed in the receiver in the shape of leaf-like crystals with a m. p. of 203°. The distillation residue of the ether solution, when treated with hydroxylamine, yielded camphoroxime, m. p. 118 to 119°. The residual oil, freed from borneol and camphor, consisted mainly of a mixture of sesquiterpenes and sesquiterpene alcohols, which, after distillation in a current of steam, boiled at about 280°.

A special interest attaches to the phenol which had been extracted from the oil by the soda liquor. It is precipitated from the alkaline solution, when acid is added thereto, in the form of a yellowish, solid body which becomes colourless after repeated re-crystallisation from benzene and petroleum ether, and melts at 82 to 83°. It is soluble in the other organic solvents. With ferric chloride it assumes a deep red colour. An elementary analysis of the phenol pointed to the formula $C_{10}H_{12}O_4$.

	Found:			Calculated for $C_{10}H_{12}O_4$:
	I	II	III	
C	60,50%	60,99%	60,75%	61,22%
H	5,85%	6,04%	6,17%	6,12%

The molecular weight determined according to Beckmann (in benzene solution) was found to be 212 (theory 196) and corresponds to the formula above. Methoxyl determinations in Zeisel's apparatus established the fact that the phenol contained two methoxyl groups: —

1. 0,3264 g. subst.: 0,8442 g. AgI.
2. 0,3046 g. „ 0,6296 g. „

	Found:		Calculated for $(OCH_3)_2$:	for OCH_3:
	I	II		
OCH_3	34,08%	27,38%	31,63%	15,81%

It was further proved by the preparation of an acetyl product as well as of a methyl derivative that the body contained a hydroxyl group.

The acetylation was carried out in the usual manner by boiling with acetic anhydride under addition of sodium acetate. The product melted at 106 to 107°, and upon combustion gave the following figures: —

1. 0,1484 g. subst.: 0,3250 g. CO_2, 0,0846 g. H_2O.
2. 0,1506 g. „ 0,3296 g. „ 0,0899 g. „

	Found:		Calculated for $C_{12}H_{14}O_5$:
	I	II	
C	59,70%	59,69%	60,50%
H	6,33%	6,04%	5,88%

The methyl derivative was obtained by boiling the sodium salt with methyl iodide in alcoholic solution. It melted at 103° and upon analysis gave the following values: —

1. 0,1505 g. subst.: 0,3443 g. CO_2, 0,0939 g. H_2O.
2. 0,1620 g. „ 0,3708 g. „ 0,1005 g. „

	Found: I	Found: II	Calculated for $C_{11}H_{14}O_4$:
C	62,37%	62,34%	62,86%
H	6,77%	6,85%	6,67%

A methoxyl determination gave the following values: —

0,3965 g. subst.: 1,3576 g. AgI.

Found:	Calculated for $(OCH_3)_3$:
OCH_3 45,37%	44,30%

Treated with bromine in a chloroform solution, the phenol forms a bromide, $C_{10}H_{11}O_4Br$, m. p. 187°. This combination crystallises from hot alcohol in yellow crystals. The bromine determination gave figures which agree with those theoretically required.

1. 0,1581 g. subst.: 0,1076 g. AgBr
2. 0,1853 g. „ 0,1270 g. „
3. 0,1770 g. „ 0,1259 g. „

Found: I	Found: II	Found: III	Calculated for $C_{10}H_{11}BrO_4$:
28,96%	29,16%	30,28%	29,09%

The preparation of an oxime from the phenol $C_{10}H_{12}O_4$ proved the still remaining fourth oxygen atom of the phenol molecule to belong to a CO-group. For this purpose the phenol was boiled for several hours with hydroxylamine hydrochloride and alcoholic potash. The oxime which separated when acid was added melted, when purified by means of dilute alcohol, at 108 to 110°. It is coloured dark-red by ferric chloride. The results of combustion agree with the formula $C_{10}H_{13}O_4N$: —

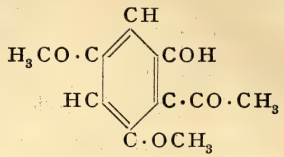
0,1532 g. subst.: 0,3170 g. CO_2, 0,0856 g. H_2O.
0,1657 g. „ 9,75 cc. N (16°, 742 mm.).

	Found:	Calculated for $C_{10}H_{13}O_4N$:
C	56,39%	56,87%
H	6,20%	6,16%
N	6,60%	6,63%

Attempts to obtain a semicarbazone remained fruitless.

From the above results it is evident that the body $C_{10}H_{12}O_4$ contains, in addition to two methoxyl groups, a ketone group, and a

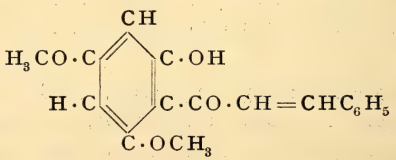
phenol group. Hence it shows, particularly also in its other physical properties, a great similarity to phloracetophenone dimethyl ether, a body first prepared from phloroglucinol trimethyl ether by Friedländer and Schnell[1]) and afterwards studied more thoroughly by von Kostanecki and Tambor[2]). As is apparent from its mode ot preparation, this body possesses the following constitution: —



Closer comparison of the phenol which occurs in Ngai camphor oil and its derivatives with the corresponding derivatives of Kostanecki's phloracetophenone dimethyl ether shows that the identity of these two phenols no longer admits of doubt, for the melting points of the phenol, its acetyl product, etc., completely agree with those of the corresponding derivatives of the synthetic phenol. Finally, the question of the identity of both bodies was clinched by the preparation of the 2-hydroxy-4,6-dimethoxychalkone, the product of condensation of phloracetophenone dimethyl ether with benzaldehyde. This combination, prepared according to Kostanecki's directions from the natural phenol, presented itself in yellow crystals, m. p. 91 to 92°, and possessed the same properties as that prepared synthetically. Combustion gave the following figures: —

	Found:	Calculated for $C_{17}H_{16}O_4$:
C	71,94 %	71,83 %
H	5,78 %	5,63 %

This body has the following formula: —



The acetyl product prepared therefrom also possessed a melting point of 130°, which is that already indicated by Kostanecki.

The trimethyl ether obtained from the phloracetophenone dimethyl ether could be oxidised with 3,3 per cent. permanganate solution at

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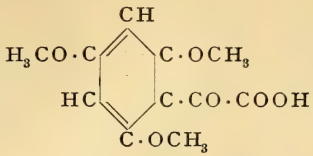
[1]) Berl. Berichte **30** (1897), 2152.
[2]) Ibidem **32** (1899), 2262.

water-bath temperature into an acid, $C_{11}H_{12}O_6$, m. p. 155,5°, of which the formula is clearly as follows: —



This acid, upon being melted, gave off carbonic acid and carbon monoxide. When submitted to dry distillation it yielded a residue melting at 49 to 50°, insoluble in sodium carbonate solution, which gave a blue colour with fuming nitric acid. Of this acid a quite considerable proportion could be obtained (36 g. from 43 g. ether) and it was easily purified by recrystallisation from hot water. It contained no water of crystallisation.

Combustion: —

1. 0,1682 g. subst.: 0,3390 g. CO_2, 0,0867 g. H_2O.
2. 0,1471 g. „ 0,2956 g. CO_2, 0,0721 g. H_2O.
3. 0,1574 g. „ 0,3169 g. CO_2. —

	Found: I	II	III	Calculated for $C_{11}H_{12}O_6$:
C	54,96%	54,79%	54,91%	55,0%
H	5,73%	5,37%	—	5,0%

The silver salt, recrystallised from water, formed colourless needles, which, however, quickly turned yellow when exposed to light.

0,1993 g. subst.: 0,0618 g. Ag.

	Found:	Calculated for $C_{11}H_{11}O_6Ag$:
Ag	31,01%	31,12%

As a ketonic acid, this acid when treated with sodium carbonate and hydroxylamine according to Bamberger's directions, yielded an oxime, m. p. 88,5 to 93°. A nitrogen determination of the body gave the following result: —

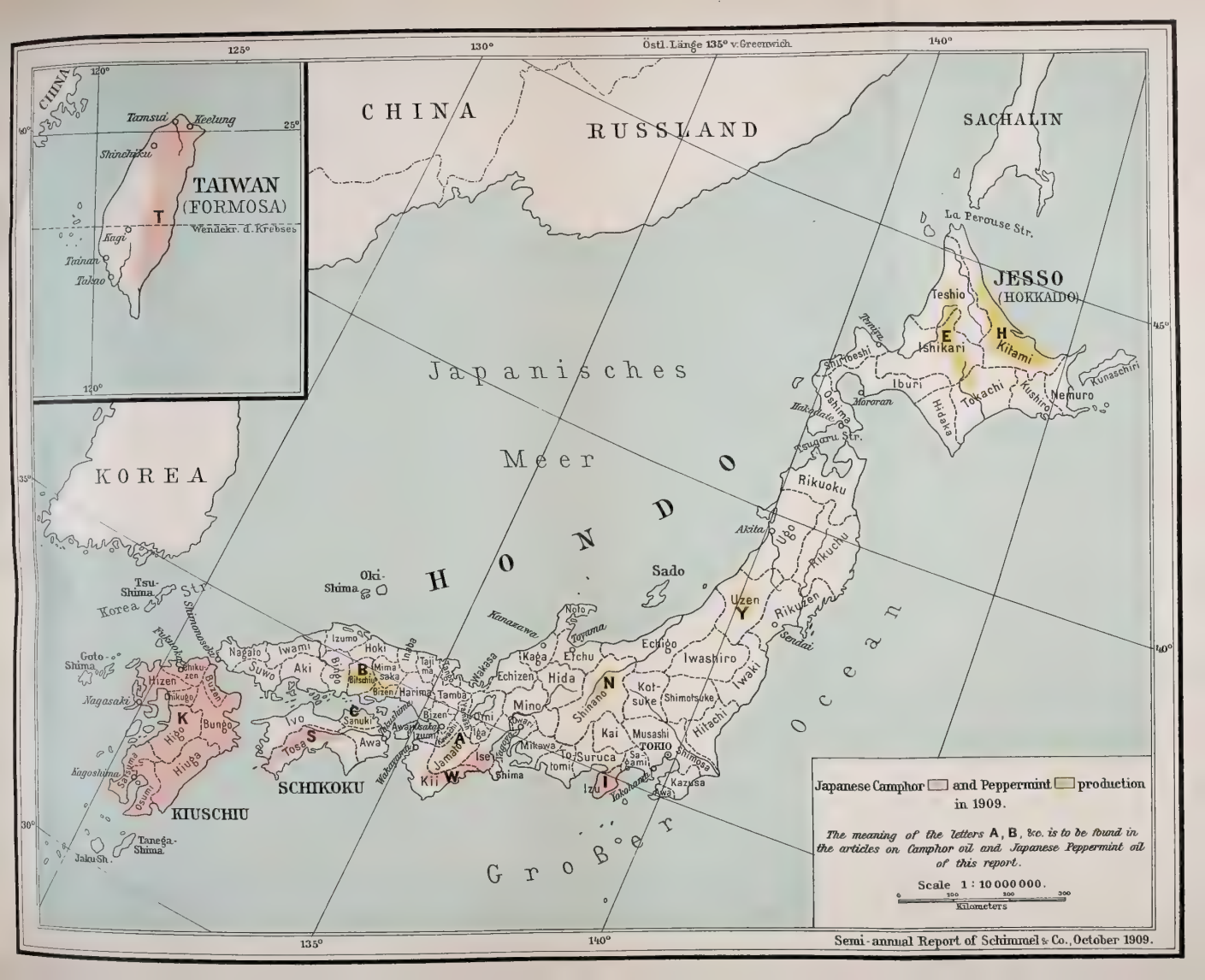
0,1444 g. subst.: 7,2 cc. N (20°, 756 mm.).

Found:	Calculated for $C_{11}H_{13}O_6N$:
5,67%	5,49%

The oxime was sparingly soluble in water and ether, but dissolved very readily in benzene.

J. J. Weber, Leipzig.

al Report of Schimmel & Co., October 1909.



Semi-annual Report of Schimmel & Co., October 1909.

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OF

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(FRITZSCHE BROTHERS)

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List of abbreviations.

d = specific gravity.

$d_{20°}$ = specific gravity at 20°, compared with water at 15°.

$d\,\frac{20°}{4°}$ = specific gravity at 20°, compared with water at 4°.

$\alpha_{D20°}$ = optical rotation at 20°, in a 100 mm. tube.

$[\alpha]_D$ = specific rotation.

$n_{D20°}$ = index of refraction at 20°.

Sol. p. = solidifying point.

M. p. = melting point.

B. p. = boiling point.

n = normal.

Acid no. = acid number; ester no. = ester number; sap. no. = saponification number.

g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

958 S335

Miltitz near Leipzig, October, 1909[1]).

When in April of the present year we reported upon the state of business in our industry, we felt it incumbent upon us to express both hopes and fears with regard to the probable development of affairs during the summer months; — hopes, because the crisis of the year 1907 could now at last be considered as overcome, and because in the United States a more confident tone in commercial life could already be felt and was bound, according to previous experience, to react upon European trade; fears, because serious expectations of war exercised a restrictive influence upon the desire to engage in business undertakings, and heavy thunder-clouds threatened to discharge themselves at the political horizon in the East. Thanks to the energetic attitude of Austria, which, trusting in the peaceful inclinations of the civilised nations of Europe, knew how to assert its authority in the imbroglio in the Balkan states, these clouds soon faded away, and in other respects our hopes have also been realised, although not in their entirety. Peace, although at one time placed in grave danger, has been maintained among the nations of Europe, and we may now look without anxiety upon the feud which is being fought out in Morocco and upon the quarrels in Crete, both of which are more or less of a local character. International commercial relations and the exchange of commodities with foreign nations are gradually returning to their normal course, and although from some of the commercial centres, such as Hamburg, the reports concerning the trade in drugs and chemicals are as yet not very cheerful, yet we should be placing the state of affairs in an incorrect light if we disguised the fact that, especially in our branch of industry, a more animated tone has become noticeable in the course of the summer.

There is every justification for anticipating a gradual but healthy improvement in the business situation in all departments of industry where our products are consumed. It is true that, up to the present time, the uncertainty respecting the financial reforms in Germany and the ultimate shape which the American customs tariff would assume,

[1]) The commercial part of this Report was compiled in September.

have had a restricting influence upon the favourable development of trade and industry, but these two obstacles having been removed, the condition of nervous tension brought about by uncertainty will again give way to a steady and purposeful striving forward. The outcome of the financial reform in Germany, it is true, has not been to the satisfaction of the industry of the country, inasmuch as the rejection of the inheritance-duty is equivalent to fresh taxation upon trade, industry, and finance, and because all these burdens, — no matter how negligible they may appear to the uninitiated — diminish our power of competition with foreign countries.

At present it is still impossible to forecast the effects of the new Spirit Excise Act, which has now come into force, upon the spirit industry, which is such an important one for the consumption of our products. We shall have to make up our minds to make the best of this Act, as we had to do in the case of the new Act on Wines which came into force on 1st September and, in various details, especially as regards the manufacture of artificial brandy, has far overshot the objects aimed at. It would lead us too far to enter here upon these subjects, which have been dealt with at sufficient length by the technical periodicals. The rejection of the projected tax on soaps and perfumery can only be received with satisfaction so far as all the interests involved are concerned, for the results of its adoption would certainly have been ominous for a considerable section of the German perfumery industry.

Our branch office at Bodenbach has again been able to record increasing sales in the Austro-Hungarian monarchy. As was expected, the dispute with Servia has been solved amicably, and the feeling of uncertainty which at the time — not without reason —, had spread itself over the whole country has again been removed, to the advantage of the general economic conditions. The alcohol industry, which is chiefly interested in our manufactures, continues to suffer severely from unfair competition, as well as from unsatisfactory manufacturing conditions, and we therefore hail with satisfaction the fact that the introduction of the projected increase in the spirit duty has again been delayed for a year. As such an increase can only take effect from the beginning of the distilling season — that is to say about the beginning of September, — and as it was not possible to bring the question to a final solution during the last session of the Austrian parliament, we are now enjoying a further term of respite of 12 months. It is to be hoped that before the conclusion of this period the branches of industry which are affected by the projected law will be able to voice their weighty objections to the new taxation in a suitable manner, and so assist in bringing about a favourable decision when the subject comes up for consideration in the next parliamentary session.

Although the declining tendency of commerce in England appears to have reached its nadir towards the end of May, and the Board of Trade returns published since June have again recorded considerable increases both in imports and exports, it would nevertheless be hardly justifiable to talk of a healthy revival of industry generally in the British Isles. Business transactions continue to be on a small scale, and much split up, and all along the line competition is exceedingly severe; nor is it possible to give any very cheerful reports of the condition of the wholesale soap manufacturing industry. Albeit that within the last few months this branch has shown a little more life, it still remains necessary to take into account an evil to which we have already called attention on previous occasions, viz., the prevalence of price-cutting, which continues to flourish most luxuriantly in this country (perhaps more so than in any other), and which renders trading in really pure articles almost incredibly difficult. The textile industry of Lancashire and Yorkshire, which is of such supreme importance for Britain from an economic standpoint, appears to show some improvement as regards the conditions of labour, but in other industries the complaints of lack of work still remain very strong; and as a further troublesome factor the agitation against the budget of the present government (a measure which has not yet been passed) must also be mentioned.

The sale of our manufactures in the British Colonies, especially in Australia and India, has moved within normal limits. In the process of fusion of the two Liberal parties in Australia, which has been effected by the new Prime-minister, Mr. Deakin, the death-knell of free-trade ideas has unfortunately been sounded, and the high protectionists have gained the victory. Although this development of affairs may have caused no surprise, yet so far as German business circles are concerned the disillusionment is not small, because the change naturally means that for Germany as well as for other countries business will be rendered more difficult, if indeed it is not diminished, in this market, which has become such a favourite outlet for many branches of manufacture. Unfortunately Germany is without any ways or means of averting the dangers of the ever-increasing protectionism, which fosters Australian industry by all imaginable means, and as the Australian Labour Party is also thoroughly protectionist, it cannot be said that pleasant times appear to be in store for German exporters. Fortunately the German chemical industry as well as our own branch produce a series of articles which must of necessity continue to be purchased in Germany, because as regards quality they stand above competition, and it is therefore to be expected that the term "Warranted to be of German manufacture" which is so often heard, will continue to exert its good repute and its power of attraction in spite of the increasing difficulties of business relations.

Our important and extensive trade with France is unfortunately threatened with serious disturbance by the new Customs Tariff Bill, the discussion of which is to be commenced after the reassembling of the Chamber of Deputies in October at the conclusion of the summer vacation. The result of these deliberations is the subject of justifiable anxiety.

In Italy industrial activity has been somewhat more pronounced. There are still firms in our branch of business which have especially selected the Italian market in order to show what they can do in the way of cutting prices, and these firms make the hearts of their Italian customers rejoice with goods of a quality which does not reflect much credit upon our German essential oil industry. Fortunately the appreciation of the value of unimpeachable service is gradually beginning to penetrate in this country also.

Nothing special can be reported as regards Spain. The spirit industry, which is the chief outlet for our manufactures, continues to suffer from the feeling of uncertainty which has been engendered by the new Spirit Act, and will only gradually be able to adapt itself to the new conditions. The burdens with which importers of our articles in Spain have been saddled by the revolution in the business conditions of this branch of industry have considerably diminished the profits and may possibly, before long, induce this or that firm to retire from the field. The extent of the disturbances which were caused in the month of July by the outbreak of fury of the masses against popish misgovernment, has been in many instances greatly overestimated abroad as a result of newspaper exaggeration, and as this season also the harvest in Spain promises to yield a favourable result, there is every ground for regarding the economic development of the country with confidence, nor is it likely that the somewhat costly adventure in Morocco, the issue of which can hardly be doubtful, will make any difference in this respect.

Russia has recently again been inclined to purchase more freely. The excellent crop prospects in most of the agricultural districts have exercised a reviving effect upon business generally, and there is every justification for cherishing high hopes of the future, judging by the result of the annual fair at Nijni Novgorod, when, as a rule, the general tendency of business finds its clearest expression so far as the prospects for the ensuing season are concerned. According to all reports, this fair has resulted in excellent business with an exceedingly strong demand for all articles of consumption. It is true that we are prevented from taking a too optimistic view of the position because of the projected revision of the Russian Customs Tariff. This revision, however, is not to be carried out purely for protective purposes, but is chiefly intended to benefit the national finances, which have been weakened by the events of the past few years.

In the spring of this year we were already able to observe that business transactions in the United States were bearing the stamp of great animation, and at the present moment we are in a position, from information supplied by our New York branch, to confirm this view so far as the summer months are concerned. In this case the question was not only one of an unwholesome increase in the turnover, such as is always to be observed on the eve of the introduction of a new customs tariff, and which in the main has its foundation in speculative undertakings, but of a sure, albeit slow revival of trade and industry after the severe trials of the last two years. The first stimulus to this improvement was given by favourable harvest prospects in the Western states. The conclusion of the customs tariff question, which occurred on 5th August by the passing of the Payne Tariff Act, has set aside the uncertainty with regard to the fiscal fate of many important raw materials which prevailed all through the course of the tariff debates, and American industry is at last able to base its calculations once more upon facts. From some sections of this great country, with its immeasurable natural resources, reports have already come in which speak of inclinations to engage in new business such as made themselves felt at the time of the boom which preceded the panic of 1907. Pronounced activity again reigns, particularly in the iron and steel industries, which are usually regarded as the barometer of the American business situation, and in many instances complaints have been heard of want of labourers. For the rest, the fact that the demand upon the banks for the supply of capital required for industrial purposes has not been especially brisk, points to a quiet development of trade. Every reasonable business man will certainly prefer these healthy symptoms to expectations of a boom.

The alterations in the Customs Tariff which affected our particular branch of industry were insignificant, and business adapted itself to the changes without great disturbances, losses, or profits.

We are glad to be able to record that in revising the separate items of the tariff, the Legislature allowed itself to be guided by the consideration that the importation of our articles, — the majority of which cannot be produced in the United States and are used exclusively for manufacturing purposes —, should not be made difficult for the consumers. We may, however, point out that, apparently as a result of an oversight, a duty has been placed upon sweet oil of orange, which has hitherto been on the free list, a circumstance which caused great surprise. The advantages which the new Act has given to the U. S. A. in business relations with the Philippine Islands are also deserving of notice. American manufactures shall be admitted into the islands duty-free, whereas upon imports from other countries

an average duty of 20% *ad valorem* must be paid. It is evident that this preferential treatment will have the effect of again drawing the attention of American business men to this colony, from the possession of which up to the present the United States have not derived much satisfaction.

Imports and Exports of Essential Oils into and from the U. S. A. in the first six months of 1909 and 1908.

	Imports			Exports	
	1909	1908		1909	1908
January	Duty-free $ 106229	$ 240624	January	Peppermint oil $ 18576	$ 29411
	Dutiable ,, 23596	,, 105102		Other indigenous oils ,, 21269	,, 14015
				Foreign oils, duty-free ,, 11587	,, 4294
				,, ,, dutiable ,, 1448	,, 1023
Febr.	Duty-free ,, 88605	,, 204003	Febr.	Peppermint oil ,, 16088	,, 21282
	Dutiable ,, 49323	,, 63302		Other indigenous oils ,, 20222	,, 23900
				Foreign oils, duty-free ,, 2448	,, 2052
				,, ,, dutiable ,, 1446	,, 515
March	Duty-free ,, 206044	,, 314612	March	Peppermint oil ,, 21674	,, 35078
	Dutiable ,, 81003	,, 41143		Other indigenous oils ,, 30436	,, 18529
				Foreign oils, duty-free ,, 2828	,, 3375
				,, ,, dutiable ,, 448	,, 1336
April	Duty-free ,, 391405	,, 201585	April	Peppermint oil ,, 12207	,, 21222
	Dutiable ,, 62971	,, 64534		Other indigenous oils ,, 27846	,, 24443
				Foreign oils, duty-free ,, 2031	,, 1031
				,, ,, dutiable ,, 1243	,, 353
May	Duty-free ,, 396076	,, 181043	May	Peppermint oil ,, 11983	,, 17221
	Dutiable ,, 60721	,, 79047		Other indigenous oils ,, 21611	,, 13429
				Foreign oils, duty-free ,, 5039	,, 1214
				,, ,, dutiable ,, 621	,, 2068
June	Duty-free ,, 207553	,, 212671	June	Peppermint oil ,, 18264	,, 15204
	Dutiable ,, 55736	,, 82306		Other indigenous oils ,, 19567	,, 16869
				Foreign oils, duty-free ,, 8218	,, 1682
				,, ,, dutiable ,, 1358	,, 598

Total value of imports in the 1st six months of 1909: $ 1729362
" " " " " " " " " " 1908: " 1789972
" " " exports " " " " " " 1909: " 278458
" " " " " " " " " " 1908: " 270144

There is nothing of special interest to report from Argentina and Uruguay. Our manufactures continue to experience a satisfactory demand, although no noticeable increase in the requirements for consumption can be recorded. Unfortunately the harvest prospects in Argentina, — a country the purchasing power of which depends mainly upon the yield of its agricultural produce, — are said to have been considerably injured by unusual drought, especially in the Southern districts. With regard to Uruguay we have no further reports, but it would seem that the climatic conditions have been more favourable there. The bill for creating the spirit monopoly which has recently been introduced in that Republic is being energetically opposed by all commercial and industrial circles as constituting an economic danger

for the country. In Brazil there has lately been talk of the introduction of a differential duty on German goods as a reprisal for the increase, in Germany, of the duty on coffee. Unfortunately this project appears to meet with much favour in Brazil, which is a matter of great regret from the point of view of the interests of German exports to this popular market.

Since our last Report no change of importance has occurred in the state of business in Chili. It is true that the creation of a special harbour police service, under the control of the customs department, in the ports of Valparaiso, Talcahuano, Iquique, and Antofagasta has brought about some degree of improvement in the conditions prevailing in those ports, which formerly defied description, but strong complaints of robbery of merchandise continue to be the order of the day. It has been ascertained by the German Consul-General n Valparaiso that these robberies chiefly take place while the goods are stored on open lighters, and on the roads. The new harbour works which have been projected for Valparaiso for some time, and the execution of which, it was thought, would do a good deal towards removing the prevailing unsatisfactory conditions, unfortunately do not appear much nearer realisation, chiefly owing to financial difficulties.

The following particulars of special interest to our branch are also taken from a report of the German Consulate referred to above: — In 1908 the value of the imports of pharmaceutical preparations and drugs amounted to $ 2686412[1]); the value of the drugs exported was $ 2940; perfumery was imported to a total value of $ 681719, mainly from France, Germany and the United States. The import value of face-powder alone amounted to $ 147188, this preparation being very popular in Chili, while $ 143568 worth of toilet soap was imported from abroad. It is said, however, that it is difficult to import soap, because it is subject to a high protective duty, and is very largely manufactured locally. There is, for instance, a large toilet soap factory in Valparaiso, which is said to have a turnover of from $ 7000 to $ 12000 monthly; and another in Santiago with a monthly turnover of $ 14000.

Interesting comparative statistics of the foreign trade (imports and exports added together) of Argentina, Brazil, Chili and Uruguay from 1892 up to 1908 inclusive have been published by the Department of Commerce and Industry of the Argentine Ministry of Commerce. These figures speak so plainly and enable us to draw such important general conclusions with regard to the development of the foreign trade and the purchasing power of the various republics concerned, that we feel compelled to place them before our readers: —

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[1]) One Peso gold = 18 d.

	Argentina Population 1908: 6489023	Brazil Population 1908: 20298297	Chili Population 1908: 3400924	Uruguay Population 1908: 1140799
	Argentine Pesos Gold:			
1892	204851500		123814866	47549760
1893	190313787	255286598	122365687	50762428
1894	194476611	217846908	118282384	61404032
1895	215164228	224066908	127760781	62100692
1896	229045607	217079306	117164936	59960464
1897	199458247	243649515	103945036	52347677
1898	241258358	261843618	102185302	59025688
1899	301768202		101820533	66707292
1900	268085481	272296150	111968429	57233080
1901	281675851	321521812	117613090	55159353
1902	282525983	304177669	120320487	61294437
1903	352191124	309738547	127291591	66971450
1904	451463494	329341617	141050648	62692000
1905	527998261	375290007	171538520	66016615
1906	562224305	434768245	197127117	72781084
1907	582065052	477310685	214755815	74329635
1908	638978077	401115466	221664205	77134957

In Peru a slight revolution, which was nipped in the bud, together with disputes with neighbouring republics, has contributed to paralyse business still more; and in Ecuador customs tariff conditions continue to prevail which make a brisk importation of our products impossible.

Unfortunately no improvement in the state of trade is reported from Mexico, which country, as a result of want of rain, has had scanty harvests, and has, moreover, been severely damaged recently by heavy floods in the north and severe earthquakes in several districts. At the same time serious political tension prevails in Mexico, now that the question of the successor of President Porfirio Diaz — who is very aged and extraordinarily popular — is becoming acute. Sanguinary encounters have already taken place between the partisans of General Reyes and those of the present Vice-President, Señor Corral.

Cuba has been favoured by an exceptionally good sugar crop, said to amount to 500000 tons, and judging by the present state of the plantations it is thought that the coming crop will exceed even this figure. Notwithstanding this there has been no improvement whatever in business, because the government of President Gomez inspires no confidence whatsoever, and there are rumours of prospective fresh intervention on the part of the U. S. A.

In Japan we have been able to observe a further slow increase in the consumption of our manufactures. In particular those oils and perfumes which are employed in soap manufacture have been in excellent demand, as the consumption of scented soaps both in Japan itself and for export from Japan, is increasing year by year. It is expected that when the revision of the treaties takes place in 1911

a heavy duty will be imposed upon European soaps, which would undoubtedly result in a greater development of the Japanese soap industry. Perfumery of the better grades is also gradually becoming more popular in Japan, and the use of scents is no longer restricted chiefly to musk, etc. The chief export market for toilet soaps is China. The boycott in Hong-Kong has not particularly affected the exportation of Japanese soaps, because the chief market for these is Shanghai, from which port the goods are forwarded further into the interior. Corea and Manchuria are gradually acquiring more importance as consumers, but the demand from Formosa still continues extremely restricted. On the other hand, the exportation of Japanese manufactures to Singapore, Colombo, Java, and India is increasing steadily, although slowly. Vladivostock has unfortunately ceased to be a customer of Japan, owing to the closing its free port, and efforts to import soaps, etc. via Kharbine have failed owing to the excessive railway freight. But as in Vladivostock itself there are two or three soap works, it is in any case probable that in the course of time the importation of Japanese soaps would have become unremunerative.

In spite of the development of the Japanese soap industry, the importation both of toilet and common soaps still continues to be considerable. According to a British consular report, the value of imported toilet soaps in 1908 was £ 41000, of which £ 16000 came from Germany, £ 10000 from France, £ 7000 from Great Britain, and £ 5000 from Austro-Hungary. Common soap was imported to the value of £ 23000, principally from France, Great Britain, and the United States.

There has been very little change in the general economic condition of Japan, and it may be asserted that the crisis, which in any case has cleared the air considerably and has resulted in the elimination of most of the unsteadying elements, may be regarded as past. Business has assumed a much more healthy tone, and, made wiser by bitter experience, all traders are careful to restrict their purchases and their stocks to the smallest possible limits. It is not likely that there will be a sudden improvement in Japan any more than throughout the rest of the world, but if the prospects of a good rice crop should be realised, the healthy gradual revival in trade is likely to make further progress. If we take into consideration that, in spite of the many unfavourable factors, such as the Chinese boycott and the depreciation of almost all produce, the economic conditions of the country have been able to maintain themselves on a tolerable basis, it is fair to assume that there is no possibility of the present state becoming worse; while, on the other hand, Japan is likely to profit from any general revival of the world's markets. We are informed that there is hardly any prospect of a serious reduction in taxes, but,

contrary to expectation, the Japanese people appear to have become accustomed to these, and the fact that such heavy burdens can be borne without dangerous weakening of the economic situation is an indication of very considerable progress in the general well-being. The fire which has taken place in Osaka is also not likely to have any permanent unfavourable effect, and the Japanese nation will soon surmount its misfortunes and flourish more than ever.

According to information received by the *Deutsche Export-Revue*, the preliminary work of the Commission appointed for the revision of the Japanese Customs Tariff was completed on 20th August at the Ministry of Finance. On the part of the Government the statement is made that in framing the new Tariff it does not wish to follow any academic principles and will neither embrace Protection nor Free Trade, its object being rather to fix the customs rates for the various articles in harmony with the conditions which prevail in Japan and in other countries. The conventional tariffs, however, are to be abolished — a measure which will result in an annual increase of about 14 millions n the customs revenues.

Before we proceed to review the various principal articles, we desire to mention that, generally speaking, the essential oil market during the period under discussion has shown but few changes, and that serious alterations in the market position were entirely wanting; hence speculative undertakings have been altogether absent. The unfavourable cold weather has not only greatly delayed the development of all the indigenous oil-plants which are used in our industry, but in most cases it has affected them so injuriously that in spite of the considerable enlargement of our cultivations at Miltitz, no increased yield can be expected as compared with the previous year. In the meantime our new distilling plant has begun to operate, but an enlargement of the building accommodation of our chemical department is now needed, and the execution of this has been projected for next spring.

Commercial notes and scientific information on Essential Oils.

Ajowan Oil. A considerable time has elapsed since any investigations were carried out as to the separate constituents of oil of ajowan seed (*Carum Ajowan* Benth. et Hook.; *Ptychotis Ajowan* D. C., Umbelliferæ). As we happened to have important parcels of the seed at our disposal we set aside 500 kilos of the mixture of hydrocarbons usually designated as "thymene" for the purpose of subjecting it to closer examination.

Previous researches[1]) had shown that thymene is a mixture of p-cymene and an unknown terpene. In order to determine the nature of this terpene it was split up into five fractions. As the b. p. increased, so the rotation, density, and refraction diminished. We investigated more closely in particular the first, third, and fifth fractions. Phellandrene (α and β) could not be detected, although this substance is a constituent of oil of ajowan herb[2]).

Of the first principal fraction we distilled 1,845 kilos (b. p. 165 to 180°; $d_{15°}$ 0,8601; α_D + 8° 41′; $n_{D20°}$ 1,48122). The bulk boiled between 170 and 175°. As the b. p. rose the rotation diminished more and more. In the fractions of which the b. p. was between 165 to 170° we were able to prove the presence of α-pinene by means of the nitroso chloride (m. p. 103 to 104°) and the nitrole benzylamine (m. p. 123 to 124°). Shaking with dilute sulphuric acid produced no hydrate; hydrochloric acid, or bromine yielded no solid additive products. The principal ingredient of the fraction was p-cymene, which was present in all the fractions of thymene. As always, we proved its presence by oxidising with permanganate into hydroxy-*iso*-propyl benzoic acid, m. p. 155 to 156°; boiled with dilute hydrochloric acid it was converted into p-propenyl benzoic acid, m. p. 159 to 160°.

The third principal fraction of the thymene showed the following constants: $d_{15°}$ 0,8574, α_D + 0° 24′, $n_{D20°}$ 1,48345. The bulk of this boiled between 179 and 181°. The rotation diminished with every further fraction. From the fractions with the higher b. p. it was easy to obtain a solid dihydrochloride possessing the characteristics of dipentene dihydrochloride (m. p. 48 to 49°). The nitrosochloride, prepared by the familiar process, had m. p. 104 to 105°; the nitrole piperidide melted at 152 to 153°. Here, therefore, we had to deal with dipentene. The principal constituent was again p-cymene.

The constants of the fifth principal fraction were as follow: b. p. 179 to 181°, $d_{15°}$ 0,8547, α_D + 0° 8′, $n_{D20°}$ 1,48054. This fraction also yielded a dihydrochloride (m. p. 52°) when hydrochloric acid gas was passed into the solution in glacial acetic acid. The fourth principal fraction yielded only liquid chlorides. The solid chloride, however, was not identical with that possessing the m. p. 48 to 49°, for both chlorides, mixed in equal parts, melted when exposed to the warmth of the hand. When hydrochloric acid was split off from both chlorides by means of aniline, the hydrocarbon from the dihydrochloride of m. p. 48 to 49° alone produced a well crystallising tetrabromide (m. p. 123 to 124°) which suffered no reduc-

[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 557.
[2]) Report October **1903**, 78.

tion of m. p. when mixed with dipentene tetrabromide. The hydrocarbon from the dihydrochloride with the m. p. 52° reacted with nitric oxide, forming terpinene nitrosite, m. p. 155°. The fraction V therefore contains terpinene, but this could only be detected in the hydrocarbon regenerated form the hydrochloride. Oxidation with permanganate gave an explanation of the problem; 140 g. of the fraction were shaken for several hours with 280 g. potassium hydroxide, 660 g. potassium permanganate, 8 kilos ice and 8 kilos water. The hydrocarbon which was not attacked consisted principally of p-cymene. From the oxidation liquors we isolated an erythritol, m. p. 236 to 237°, which proved to be identical with that obtained by Wallach [1]) in the oxidation of terpinene preparations. Wallach is of opinion that this erythritol is formed from $\Delta_{1,4}$-menthadiene (γ-terpinene). No α,α'-dihydroxy-α-methyl-α'-*iso*propyladipic acid was detected. Boiled with diluted sulphuric acid, the erythritol gave off water, and a phenol mixture was formed consisting of equal parts of thymol and carvacrol [2]). Thus we arrive synthetically from thymene to thymol, which latter, as is well known, forms the principal constituent of ajowan oil.

The fifth principal fraction, therefore, consists mainly of γ-terpinene and p-cymol only. The non-occurrence of the nitrosite-reaction also agrees with this result, for in Wallach's opinion the terpinene nitrosite is formed from α-terpinene only. On the other hand, Kondakow [3]) has recently expressed the opinion that the nitrosite is a derivative of γ-terpinene. We will not venture to decide in how far these views are correct: in any case we failed to succeed in isolating terpinene nitrosite. It may be, of course, that the separation of terpinene-nitrosite is prevented by the presence of p-cymene.

It follows that thymene is mainly made up of p-cymene. Of terpenes, α-pinene, dipentene, and γ-terpinene were found to be present, the latter in the largest proportion.

Almond Oil, pressed from apricot kernels. Since the publications of our last Report concerning apricot kernels the price remained about at its present level until the month of May, the tendency being firm. At that time, however, the almond prices suddenly began to rush up and the market for apricot kernels followed suit, the quotations for the Damascus variety advancing up to 86 to 88 marks, while Californian apricot kernels advanced as high as 96 to 98 marks. The two chief trading centres, Marseilles and Hamburg, made every effort to reap as much profit as possible from these quotations, but the consumers

[1]) See Report November **1908**, 174.

[2]) Comp. Gildemeister and Müller, Zur Kenntnis der Bestandteile des Citronenöls. Wallach Jubilee-publication. Vandenhoek & Ruprecht, Göttingen, 1909. When this publication is issued to the public we propose to revert to its contents.

[3]) Journ. f. prakt. Chemie II. **79** (1909), 497. See also the present Report, p. 171.

did not respond freely, and as a result the market gradually receded to 75 marks for Damascus, and to 84 marks per 100 kilos for Californian kernels, under the pressure of a lack of demand. In the meantime the article has remained at the above quotations, but there is a well-founded prospect that in the course of the autumn when, as experience shows, apricot kernels are always in the best demand, the market will again rise. For the present it is true that business is still slack, but it is said that there is already some indication of a desire to buy for later shipment. It must be borne in mind that according to report, cocoa-nuts and ground-nuts have lately been used as substitutes for sweet and bitter almonds for many purposes, but these products will never be able to take the place of apricot kernels altogether.

This year's crop in the district of Damascus is reported to have been a fair average one, but in the other apricot districts of Asia Minor the results have only been very meagre, especially because these regions have been severely tried by serious disturbances which happened to synchronise with the harvest time. From California the reports were at first very favourable, but there also, it now appears, only a moderate harvest can be reckoned upon. The output of Japan, of which there has been a good deal of talk lately, is quantitatively so slight that it cannot be expected to have any influence whatsoever upon the course of the market.

As is always the case, the sale of pressed almond oil from apricot kernels has dragged somewhat during the summer months, but the fact that almond oil from sweet almonds has recently considerably advanced in price has rather stimulated the demand for the first named variety. The sale of essential oil of bitter almonds of our own distillation has been of normal proportions.

Almond Oil, pressed, from almonds. Ph. G. IV. In the course of the summer the prices for all varieties of sweet almonds had advanced greatly, because the fears of a considerable shortage in the crop in all producing districts (which had already been expressed in our last Report) were confirmed, and at the beginning of September a sudden further upward movement took place, bringing the prices of first quality Sicilian almonds up to 230 marks and for Bari quality up to 215 marks per 100 kilos. The Sicilian harvest is said to have yielded an even worse result than had been expected. It is said that it will amount to only about 20 000 bales, while the whole of last year's stock has been cleared. In Apulia, it is alleged, the crop will be less than half of the average. If we take into account that in the spring sweet almonds averaged about 150 marks per 100 kilos, it will be seen that there is no further need to explain the important increase which we have been compelled to make in the price of pressed

almond oil. Our sale has been exceptionally brisk at full quotations, and at times we have only been able to satisfy the demand after considerable delay.

In an earlier Report[1]) we pointed out that efforts have lately been made in the United States to manufacture within the States certain oils which up to the present have been purchased abroad. Among these is oil of almonds, both of the fatty and of the essential variety, which, as is well known, are not prepared from almonds but from the stones of plums, apricots and peaches. A report by F. Rabak[2]), published by the United States Department of Agriculture, contains other information which may be of interest to fruit growers in the United States. In the introduction, which is chiefly botanical, Rabak gives the following details with regard to the cultivation of the fruits referred to: —

Apricots are chiefly grown West of the Rocky Mountains. Peaches occur very widely, chiefly in California, Colorado, Michigan, Georgia, Missouri, Arkansas, Texas, Delaware, Maryland, West Virginia, and New Jersey. Plums grow particularly in California, Oregon, Washington, and Idaho. The almond tree has been introduced into California, where the climate appears to be particularly favourable to its growth. The output of fruit has increased greatly during the last few years. The value of exported dried fruit in 1906 was as follows: —

Apricots	$ 1325422
Peaches	„ 110407
Plums	„ 1410636[3])

With the object of determining to what extent American material might be used for the production of the fatty and essential oils mentioned above, almonds, plum, and peach kernels were extracted with ether in order to obtain the fixed oil. Rabak found that sweet and bitter almonds contain a little more fixed oil than the other kernels. The specific gravity was practically the same for all oils, and moreover there was scarcely any difference in colour, odour, taste, or congealing point. The same applies to the saponification, iodine, and acid numbers, and the elaidin test[4]) also gave similar results for all the oils.

The yield of essential oil was not equal for the different kernels; peach kernels yielding 0,7 %, apricot kernels 1,6 %, plum stones 0,3 to 0,46 %, and bitter almonds 0,81 %. No great accuracy, however, can be claimed for these figures, because only small quantities of material (0,6 to 1 kilo) were used, and because the complete separation of the small quantities of oil produced was rendered more difficult by

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[1]) Report November **1908**, 154.
[2]) U. S. Department of Agriculture, Bureau of Plant Industry, Bulletin 133, **1908**.
[3]) Commerce and Navigation of the United States **1906**, 596.
[4]) U. S. Pharmacopœia, 5th edition (1905), p. 307.

their comparatively ready solubility in water. Here also the physical and chemical constants were in close agreement, only the benzaldehyde-content varied from 61,8 to 88,7 %, and, except in the case of an oil distilled from plum kernels, which had 88,7 % of aldehyde, remained below the minimum content of 85 % required by the Pharmacopœia. This low content Rabak also attributed to the fact that the quantities used were too small and were readily liable to oxidation. According to an estimate, the total annual production of kernels in the State of California and of the oil which might be prepared from them, would be as follows: —

	Kernels	Pressed oil	Essential oil
Apricots	5000 tons	400 to 500 tons	18000 to 22000 lbs.
Peaches	10000 „	210 „ 420 „	7800 „ 15600 „

In conclusion, Rabak calls the attention of fruit growers in the United States to the fact that, instead of throwing away the stones or using them as fuel, as at present, they might with greater advantage use them for the production of these valuable oils.

A continuation of the paper discussed in our previous Report[1]) is supplied by the second treatise of L. Rosenthaler[2]) on asymmetric syntheses produced by enzymes. The author has investigated the effect of foreign bodies upon the rotation, which occurs in the benzaldehyde-hydrocyanic acid-emulsin system. In every experiment he diluted equal parts of benzaldehyde, hydrocyanic acid, and emulsin with alcohol, formaldehyde, metallic salts, and so forth, and compared the rotation observed unther these conditions with that shown by the same quantities of experimental material *minus* the added foreign bodies, but under otherwise equal conditions. The following, generally speaking, had but a slight deteriorating effect (i. e. did not greatly reduce the altitude of rotation) viz., alcohol (even if added in comparatively large proportions), 1 % phenol-solution, formaldehyde, ammonium sulphate, magnesium sulphate, hydrogen sulphide, manganese sulphate, and hydrogen ferrocyanide. On the other hand, the following produced deteriorating results, viz., sulphate of copper, acetate of lead and oxide of mercury, as well as H- and OH-ions. In fact, OH-ions entirely prevent the generation of optically active substances, whereas H-ions only act injuriously. Pepsin and trypsin are injurious in neutral solution. Further, s-emulsin[3]) is precipitated by picric and tannic acids. From these experiments, Rosenthaler concludes that, on the whole, s-emulsin behaves like an albumen, by which, however, he must not

[1]) Report April **1909**, 17.

[2]) Biochemische Zeitschr. **1909**, 257. From a reprint kindly sent to us.

[3]) The constituent of emulsin which influences the synthesis, Rosenthaler calls syn- (s-) emulsin; that which hydrolyses he calls dia- (d-) emulsin.

be understood as maintaining that it *is* in fact an albumen. But it differs from the albumens only in not being precipitated by hydrogen ferrocyanide (ferrocyanide of potassium + glacial acetic acid).

Rosenthaler also reports on experiments with emulsin made by him on a series of aldehydes and ketones in order to determine whether emulsin

1. is capable of producing the asymmetrical addition of hydrocyanic acid to the aldehydes and ketones.
2. has a general effect of hastening the absorption of hydrocyanic acid.
3. affects the equilibrium of the reaction.

The table which accompanies the paper shows that most aldehydes yield active, and the ketones only inactive, hydroxynitriles. The following yield dextro-rotatory nitriles: acetic aldehyde, *iso*butylic aldehyde, heptylic aldehyde, octylic aldehyde, furfurol, o-methoxybenzaldehyde, anisic aldehyde, cuminol, piperonal, o-nitrobenzaldehyde, cinnamic aldehyde, phenyl acetic aldehyde, *iso*phthalic aldehyde, terephthalic aldehyde. Citral and o-phthalic aldehyde yield lævorotatory nitriles, and the following yield inactive nitriles: chloral, salicylic aldehyde, m-hydroxybenzaldehyde, p-hydroxybenzaldehyde, p-nitrobenzaldehyde, methyl-ethylketone and acetophenone.

In his experiments on the displacement of the equilibrium of reaction towards the nitriles, Rosenthaler met with experimental difficulties which he ascribes to the fact that commercial emulsin contains both s- and d-emulsin. He hopes, later on, to be able to repeat his experiments with s-emulsin of the greatest possible purity.

The views expressed by Rosenthaler to which we made reference in our last report[1]), and which are confirmed in the paper quoted above, and amplified by the examples cited therein, are endorsed by S. J. M. Auld[2]). That investigator, on the basis of experiments of which the results have lately been published, concludes that (assuming primarily benzaldehyde-cyanohydrin to be formed at all when amygdalin is split up by emulsin), such a formation can only take place to a limited extent and for a short period. Parallel-experiments in the splitting-up and synthesis of benzaldehyde from amygdalin, or the constituent under the influence of emulsin, showed that the synthesis proceeds much more rapidly than does the decomposition. For instance, a solution of 2 g. of amygdalin and 0,2 g. emulsin in 50 cc. water was extracted with ether after standing for 3 hours. The evaporation-residue dissolved in chloroform had a rotation of + 0° 9′, while 2 g. benzaldehyde, 0,8 g. hydrocyanic acid and 1 g. emulsin, dissolved in 50 cc. water and treated in the same manner, after 3 hours had a rotation of + 0° 51′.

[1]) Biochemische Zeitschrift **1908**, 238; Report April **1909**, 17.
[2]) Journ. chem. Soc. **95** (1909), 927.

Furthermore, the action of emulsin upon artificial benzaldehyde cyanohydrin was investigated. 11 g. of the synthetically prepared nitrile, which was faintly lævorotatory, was kept for three days with 50 cc. water and 0,5 g. emulsin at ordinary temperature, then extracted with ether, the residue of evaporation dissolved in 100 cc. chloroform and its optical behaviour tested in a 2 decim. tube. It was found to show a rotation of + 0°36′. The aqueous solution contained 0,09 g. hydrocyanic acid. As a check-test the experiment was repeated, but without the addition of emulsin. In this instance the rotation observed in a 2 decim. tube was —0°5′ and the hydrocyanic acid-content was 0,05 g. According to Auld these experiments prove that the cyanohydrin is first split up and that subsequently, under the influence of emulsin, asymmetric synthesis may take place.

Recent observations made by Feist[1]) contradict the views quoted above. In a paper published very shortly after the appearance of that of Auld, Feist dealt with the preparation of the two optically active benzaldehyde cyanohydrins. The lævorotatory isomeride was obtained, after many fruitless experiments, from artificial, inactive oil of bitter almonds (containing prussic acid), of which the rac. benzaldehyde-cyanohydrin content was ascertained at 80,8 %. This cyanohydrin was allowed to stand, in dilute alcoholic solution, with emulsin for 48 hours at 20° with occasional stirring, while for the purpose of removing the prussic acip a current of air was passed through. The explanation of the reaction (which is based upon the fact that, to all appearance, emulsin only splits off d-benzaldehyde cyanohydrin) is that the conversion expressed in the following equation is partly accomplished: —

(d + l)-benzaldehyde cyanohydrin + emulsin = l-benzaldehyde cyanohydrin + benzaldehyde + hydrocyanide + emulsin.

The liquid was extracted with ether, the evaporation residue weighed, again dissolved in ether and tested as regards its rotatory power, which was found to be α(?[α]) — 1,4°. When the l-benzaldehyde cyanohydrin was heated with hydrochloric acid, d-mandelic acid was produced.

Feist also investigated the formation of d-benzaldehyde cyanohydrin in the breaking-up of amygdalin and observed that this proceeds quantitatively. Other experiments consisted in preparing benzaldehyde cyanohydrin from amygdalin by means of emulsin by splitting-up, and then producing it synthetically by means of emulsin under similar experimental conditions from hydrocyanic acid, benzaldehyde and glucose, in proportions equivalent to amygdalin. The results thus obtained confirmed Feist in the view he had previously expressed[2])

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[1]) Arch. der Pharm. **247** (1909), 226.
[2]) Arch. der Pharm. **246** (1908), 206; Report November **1908**, 14.

that amygdalin, when treated with emulsin, yields primarily d-benzaldehyde cyanohydrin, because the products obtained in the splitting-up process were almost all more strongly dextrorotatory than those prepared synthetically.

It will be seen that the results obtained by Feist are in sharp contradiction to those of Auld.

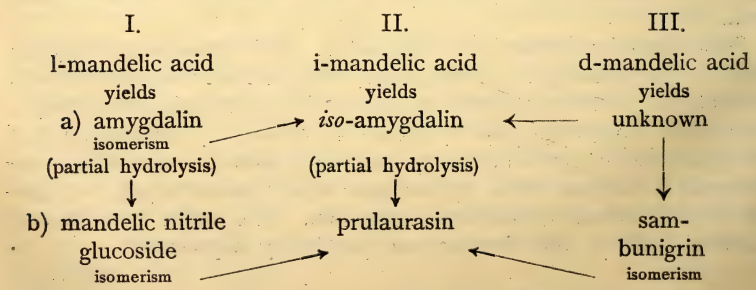
Further experiments by Feist served to solve the problem whether (as had previously been assumed to be the case), water produces a racemisation or a decomposition of d-benzaldehyde cyanohydrin. It was found that pure cyanohydrin preserved its originally ascertained rotation of $[\alpha]_D + 14{,}0°$ even after 20 days. But if, of the same cyanohydrin, 2 g. which, when dissolved in 10 cc. ether, showed a rotation of $+ 2°$ (in a 1 decim. tube), was left, after evaporation of the ether, for 8 days in contact with 100 cc. water under occasional stirring, the cyanohydrin, when once more dissolved in ether, had a rotation of $+ 0{,}5°$ (in a 1 decim. tube). In this experiment hydrocyanic acid could not be detected in the aqueous solution, so that in any case no decomposition had occurred.

Upon comparing those glucosides known up to the present, which, when decomposed, yield benzaldehyde and hydrocyanic acid, it will be found (as stated by E. Bourquelot[1]) at the VII. International Congress for Applied Chemistry), that these bodies may be divided into two classes, viz., those which, when hydrolysed, form one, and those which form two, molecules of glucose,

a) 2 mol. glucose: — amygdalin and *iso*-amygdalin,

b) 1 mol. glucose: — mandelic nitrile glucoside, prulaurasin and sambunigrin.

Taking into account the rotation of the mandelic acid which is formed during decomposition, as well as the products resulting from treatment with baryta, the following table may be drawn up to show graphically the mutual relationships of the above-named glucosides: —



[1]) Journ. de Pharm. et Chim. VI. **29** (1909), 576.

A hitherto unknown glucoside may therefore be expected, which, when isomerised with baryta yields *iso*-amygdalin, when completely hydrolysed, d-mandelic acid, and, when partially hydrolysed, sambunigrin.

The isomerisation of amygdalin into *iso*-amygdalin indicated in the above table was discovered in 1904 by H. D. Dakin[1]), who obtained the conversion by treatment with diluted alkalies in the cold. Fresh communications by F. Tutin[2]) are now available, the upshot of which is that *iso*-amygdalin consists of a mixture of two glucosides, viz., amygdalin and neo-amygdalin.

Tutin prepared *iso*-amygdalin from amygdalin by allowing it to stand with highly diluted ammonia. The mass having been evaporated to a very thick syrupy consistency, it was at once acetylated, without previous isolation of the *iso*-amygdalin. The heptaacetylamygdalin, recrystallised from alcohol, had a m. p. of 166 to 167° and a spec. rot. of $[\alpha]_D$ —37,6° (in chloroform).

By adding a little alcohol to the crude product of acetylation, diluting the solution with ether, and extracting with water, there was obtained from the ethereal solution a product which crystallised in long, colourless needles and possessed the following constants: — m. p. 174° (from alcohol), $[\alpha]_D$ —65,6° (in chloroform), —57,1° (in acetic ester). The author calls this body hepta-acetyl neo-amygdalin.

Upon hydrolysis the new glucoside yields d-mandelic acid.

Up to the present no investigations had been made with the object of determining the process of the hydrolysis of amygdalin by the use of various acids. It was tacitly assumed that they would all have a decomposing action, and that, as is the case with hydrochloric acid, the glucoside, when treated with diluted acids, would yield, in addition to glucose, hydrocyanic acid and benzaldehyde, and, when concentrated acids were employed, mandelic acid and ammonium chloride. Investigations which have lately been made into this subject by W. Walker and V. K. Krieble[3]) have shown, however, that this supposition is incorrect. When amygdalin was heated for $1^1/_4$ hours with moderately strong concentrated sulphuric acid (2 g. sulphuric acid to 6 g. water) it yielded almost the theoretical quantity of benzaldehyde cyanohydrin, while, when treated with dilute sulphuric acid and heated for 2 hours at 98°, the decomposition process was found to have only reached the stage of formation of l-mandelic nitrile glucoside. Concentrated aqueous oxalic acid solution behaved similarly to diluted

[1]) Journ. chem. Soc. **85** (1904), 1512.
[2]) Ibidem **95** (1909), 663.
[3]) Ibidem **95** (1909), 1369.

hydrochloric acid. But the behaviour of trichloroacetic acid was most surprising, this agent having no decomposing effect whatsoever. This is the more remarkable when it is remembered that trichloroacetic acid is almost as highly dissociated as is hydrochloric acid.

Angelica Oil. In connection with what was said in our last Report, we are able to state that the prices have not only been maintained, but have even further advanced to about 150 marks for pure distillate from *roots*, owing to the decrease of stock. The circumstance that the price has not exceeded this figure is due to the fact that quite recently, in anticipation of the new root crop (which however is not due until next month) the consumption, quite properly, has been restricted. It is generally known that the cultivations in Thuringia have been very considerably extended, and according to the reports to hand the prospects are exceedingly favourable.

Our Miltitz cultivations also promise to yield an increased harvest. It is certainly to be wished that the scarcity which has now prevailed for 2 years will at last be brought to an end, and that this important oil will again be placed on the market at reasonable prices.

In angelica *seed*, however, lower prices are scarcely to be expected, and we are as yet unable, therefore, again to include this oil in our lists.

Anise Oil. At the time when this Report was compiled, no detailed information regarding the present season's crop in Russia was yet available, the reason being that the gathering of anise, as well as of other produce, has suffered considerable delay owing to the unfavourable weather which has prevailed throughout the summer. Although the area under cultivation this year has been less than in 1908 by about 500 dessiatines, the total output is expected to be about 200000 poods, and may therefore be regarded as a favourable one. The first aniseed fair was held at Krasnoje on 15th September. Very large supplies had been expected, because sunflower seed, which in normal times always commands the chief interest at the first fair, has yielded an unusually scanty crop this season. Notwithstanding this fact, and contrary to expectation, little was offered, and the presence of numerous speculators caused the holders to demand very elevated rates. It will probably be impossible to express any definite opinion as to the value of the article during the current season until the second aniseed fair is held. The samples to hand show the quality of the new seed to be a middling one; fine green seed is likely to be again a rarity, for the great heat of the last few weeks has somewhat damaged the growing crop. The seed is smaller and darker in colour than had been expected.

Oil of Apocynum androsaemifolium. The rhizome of *Apocynum androsæmifolium* L. (Apocynaceæ), a native of North America,

has been subjected to a thorough examination by C. W. Moore[1]). By distilling the alcoholic extract with steam a small quantity (3 g. from 19 kilos rhizome = 0,016 %) of an essential oil of pale yellow colour and strong, persistent odour, was isolated. This oil was found to possess the following constants: $d\frac{12°}{12°}$ 0,948, b. p. 130 to 250°, α_D + 0° 50'. The oil gave a strong furfurol-reaction. Aceto-vanillone, $CH_3O \cdot C_6H_3(OH) \cdot CO \cdot CH_3$ (m. p. 112 to 114°) was also detected in the distillate. This body was obtained in considerable proportions from the non-volatile part of the alcoholic extract of the rhizome, partly also in the from of aceto-vanillone glucoside, $CH_3 \cdot CO \cdot C_6H_3OCH_3 \cdot O \cdot C_6H_{11}O_5 + 2\,H_2O$. This is a new glucoside, to which Moore gives the name of "androsin". It dissolves readily in hot water and in hot dilute alcohol. The fact that it is hydrolysed by emulsin shows it to be a β-glucoside. The author also isolated from the rhizome a series of other bodies, which, however, do not belong to the constituents of essential oils and are therefore outside our sphere of interest.

Arnica Oil. We are again able to supply an exquisite freshly distilled oil from *flowers*, although there was some difficulty in procuring suitable distilling material. We were also able at the proper time again to replenish our stock of arnica *root* oil.

Kondakow[2]) has lately made an investigation of arnica root oil. From this oil he succeeded in isolating an unsaturated hydrocarbon, m. p. 176 to 180°, a solid body (m. p. 69°), and a sulphurous compound. He was able to confirm the presence of *iso*-butyl phlorol and dimethylthymohydroquinone, which had already been discovered in the oil by Siegel[3]).

Oil of Artemisia Herba-alba var. densiflora. We have recently again distilled a parcel of the herb of this plant, to which reference was made in our last Report[4]), and obtained a yield of 0,58 % of oil, which differs in several respects from that described last. It is also of a brownish-yellow colour and is distinguished by a pungent odour, which was only perceptable in a slight degree in the former sample. On the other hand, in the recently-distilled sample the odour of thujone or sage does not appear until some time after preparation. But the principal difference lies in the change of optical rotation, for whereas the old oil was lævorotatory, the new sample is dextro-

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[1]) Journ. chem. Soc. **95** (1909), 734.
[2]) Journ. f. prakt. Chem. II. **79** (1909), 505.
[3]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 688.
[4]) Report April **1909**, 98.

rotatory; it also contains considerably more alcoholic constituents than did the old oil. All these variations may perhaps be explained by the fact that the oil distilled last year was prepared from the flowering herb, whereas on the present occasion the flowers were very little developed. The constants of the new sample are as follow: — $d_{15°}$ 0,8994, α_D + 14° 5′, $n_{D\,20°}$ 1,46684, acid no. 4,6, ester no. 35,0, ester no. after acetylation 163,3; dissolves in 1,8 vol. and more of 70 per cent. alcohol, with separation of paraffin.

Basil Oil. Although several new sources of production of this article have been opened up of late, the supplies are still restricted to trifling quantities, and the price therefore almost remains at its previous level. One of our suppliers in Algeria has unfortunately been unable to fulfil his contract in its entirety because, as a result of the unfavourable weather, his output has fallen considerably below his expectations. From Réunion also only very moderate quantities have come into trade.

A few years ago an essential oil from *Ocimum Basilicum* L. (Labiatæ), of the variety known as *"selasih hidjau"* was distilled at Buitenzorg [1]), Recently van Romburgh has prepared a considerable quantity of this oil, which he has submitted to a fresh examination, in completion of his previous publication on the subject [2]). The oil was found to possess the following constants: $d_{14°}$ 0,962, opt. rot. in a 2 decim. tube + 1° 20′. Out of 1500 cc. of oil, 210 cc. were separated by steam-distillation, and this, when distilled *in vacuo* (? mm) yielded the following fractions: —

75 cc., b. p. up to 88°, [α (+?) 9° 17′ in a 2 decim. tube]
105 cc., b. p. 88 to 93°, [α (+?) 1° 16′ in a 2 decim. tube]
Residue: 26 ccm.

The first fraction was distilled again, when 28 cc. boiled below 70° (d 0,856) and 63 cc. at between 70 to 85°. (A printer's error must have occurred here, for 28 + 63 = 91, whereas only 75 cc. were distilled). From the portion with the lowest boiling point, cineol was isolated by means of resorcinol-solution, after which it was more particularly identified by the iodol-test. The fraction 70 to 85° was fractionated *in vacuo* (? mm) after removal of the cineol, when finally a small quantity boiling from 60 to 70° was obtained, the density ($d_{15°}$ 0,8208) and odour of which seemed to point to the presence of an olefinic terpene.

The methylchavicol obtained from the Javanese basil oil rotated, in a 2 decim tube, (+?) 1° 30′. Various attempts to remove its active

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[1]) Report April **1901**, 12.

[2]) Koninklijke Akademie van Wetenschappen te Amsterdam, **1909**, 15. From a copy kindly sent to us.

principle by means of acetic anhydride, sodium bisulphite, permanganate etc. were fruitless; only by treatment with magnesium ethyl-iodide the methylchavicol could be obtained in inactive state; it boiled at 214 to 215° (corr.). After being heated for 48 hours to 250° in sealed glass tubes and left to stand in the cold, crystals separated out from the distillation residue (temp. in the liquid 240°). These crystals, when purified from acetone and alcohol, melted at 98°. In addition, there was obtained a body of m. p. 166°. Both, when dissolved in petroleum ether or benzene, gave a blue fluorescence. The elementary analysis indicated methylchavicol; the determination of molecular weight showed that both bodies consisted probably of double molecules of methylchavicol. From the compound melting at 98°, an additive product of bromine with the formula $C_{20}H_{24}O_2Br_2$ could be obtained. The examination is being continued.

From Anjouan, one of the Comoro islands, we have received a sample of basil oil which, in its properties, resembled the Réunion oils. Like these, it had a high sp. gr., $d_{15°}$ 0,9608, its optical rotation was to the right, α_D + 0° 40′, and it possessed a high index of refraction, $n_{D\,20°}$ 1,51425. It gave a clear solution with 5 vols. of 80 per cent. alcohol, which remained unaltered when diluted.

Bay Oil. The past months unfortunately have brought no improvement in the position of this oil, which was once an article of so much importance. The demand continued to drag, and we regret again to be compelled to state that in spite of its many excellent qualities, bay rum, formerly so popular, appears to be less used than previously. This notwithstanding, there are quite a large number of customers for our terpeneless bay oil.

The Imperial Institute in London has sent us two samples of bay-oil produced in the Fiji islands, which were found to possess the following constants: —

a) $d_{15°}$ 0,9893, α_D — 1°, phenol-content 23%. Soluble in 0,3 vols. and more of 90 per cent. alcohol.

b) $d_{15°}$ 0,9605, α_D — 2° 10′, phenol-content 24%. Soluble in 0,3 vols. and more of 90 per cent. alcohol; when diluted, the solution became opalescent.

As compared with the normal commercial oils, which contain about 60% of eugenol, the two samples show an exceptionally low phenol-content, which may be due to the manner of manufacture. In the course of the distilling-process one part of the bay oil separates out on the surface of the receiver, while the other sinks to the bottom; hence, if a normal oil is to be produced, these two parts must be carefully mixed after distillation. If this is neglected, the result

is that the oils obtained are sometimes too light, and at other times too heavy, because, owing to unworkmanlike distilling, they lack some portion of either the light or the heavy oil. It may therefore be surmised that in the case under review a similar mistake was made during the distillation.

The low specific gravity of the second sample corresponds to the slight phenol-content, while the unusually high sp. gr. of the first-named oil, in conjunction with its low eugenol-content, was most probably the result of oxidation (polymerisation) processes.

In continuation of what we stated in our last Report[1]) on Lemon-scented Bay Oil, we may now state that some time ago we received from the West Indies a consignment of leaves called Citronella Leaves. These were subjected to careful botanical examination, when it was found that in addition to the genuine bay leaves from *Myrcia acris* D. C. (Syn. *Pimenta acris* Wight)[2]), *Pimenta acris* Kostel., *Eugenia acris acris* Wight and Arnott, it contained those of two closely allied species. In addition to the variety yielding lemon-scented bay oil *Pimenta acris* var. *citrifolia* (*Myrcia pimentoides* D. C., *Pimenta citrifolia* Kostel.) it also contained leaves of *Myrcia coriacea* D. C. As the material was not uniform we have for the present abstained from distilling the oil.

Birch bud Oil. An oil distilled by us this season from birch buds possessed more or less the same constants as the sample previously described[3]), which was also of our own distilling. The odour was pleasantly balsamic, the colour lemon-yellow, and the sample contained a large proportion of paraffin, crystals separating out plentifully at $+ 8°$, while at $+ 5°$ it was completely congealed. Its other properties are as follows: $d_{15°}$ 0,9730, α_D $— 5° 34'$, $n_{D\,20°}$ 1,50153, acid no. 2,8; ester no. 51,4 = 24,1 % acetate of a sesquiterpene alcohol of the formula $C_{15}H_{24}O$. Ester no. after acetylation 150,0, corresponding to 66,4 % total alcohol $C_{15}H_{24}O$. 0,25 vol. of 90 per cent. alcohol was sufficient to dissolve the oil, but when more alcohol was added a plentiful separation of paraffin set in quickly.

Cajeput Oil. Business in cajeput oil has continued to be very slow, and the numerous offers of oil in store in Europe confirm our surmise that the article is no longer in as much demand as formerly. It is a matter for congratulation that the exporters are taking account of this fact by restricting their shipments, for according to the statistics

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[1]) Report April **1909**, 21.

[2]) The opinion of Holmes, which is also reproduced in Gildemeister's and Hoffmann's book *The Volatile Oils*, p. 510, that *Pimenta acris* Wight and *Myrcia acris* D. C. are not identical, is not agreed with by all botanists.

[3]) Report October **1905**, 13.

from Macassar the exports in the months of January to May have been as follows: —

1909	731	baskets
1908	1386	„
1907	1752	„
1906	1061	„
1905	1408	„

Naturally prices have been very depressed, the general endeavour of all holders being to get rid of their stocks as soon as possible.

Camphor Oil. There is not much to say concerning the market position of this important article. It is true that during the past few months, owing to the firmness of the turpentine market, the demand has been fairly brisk, and from the East we are informed that the entire production up to the beginning of this month is said to have been sold to the United States. But notwithstanding all this, we are inclined to think that there will be no serious alteration in price in the near future. As there has been no change in the import duty on oil of camphor in the new American Customs Tariff, it seems likely that the demand from the United States will soon fall off.

In Europe there is an ample stock, which will suffice for a considerable time and is difficult of sale, while its cost is partly very high. The firmer tone which has been felt in the camphor market during the past few months has so far been without effect upon the price of camphor oil. As already mentioned, our light camphor oil is particularly deserving of increased interest owing to the fact that it is a cheap substitute for oil of turpentine; and we take this occasion of reminding our readers that with our perfect manufacturing plant we are able to comply with every wish as regards the specific gravity of the oil, provided the order be sufficiently large.

This year's camphor output in the whole of the Japanese Empire (see map at the end of the present Report) is estimated by our informant as follows in each of the different districts: T (Formosa) 5 million kin; K (Kiushiu) 850000 kin; Hondo (S = Tosa 20000 kin; W = Kii, Ise, and Shima 20000 kin; I = Izu 10000 kin) 50000 kin; total 5 900 000 kin = approximately 7 870 000 lbs.

Concerning the movements of the camphor market in Japan, the *Oriental Physician and Druggist* of 1st June 1909, Vol. 3, No. 7, page 1, gives the following particulars: —

In spite of the reduction of the camphor price to 80 yen per 100 kin, which was made by the Government in October 1908, the market did not revive, and the position of the camphor industry only improved when the financial condition in the West became more satisfactory.

The exports in the first quarter of the past 3 years have been as follows: —

	Kin	Yen
1907	614000	713826
1908	391000	450935
1909	1666850	1481049

The exports in 1909 were divided as follows among the various countries concerned: —

	Kin	Yen
England	221000	205316
France	386000	374998
United States	540750	488775
Germany	494000	407800
British India	24200	4160

The exports of camphor from Formosa and from Japan during the last 4 years are stated as follows in a report[1]) of the German Consul at Nagasaki: —

	Formosa		Japan	
	Kin	Yen	Kin	Yen
1908	2073550	2218706	1807565	2063410
1907	3090950	3567449	3057657	5026858
1906	2789394	2822871	2656581	3632785
1905	2923117	2683522	2284794	2566232

The report[2]) of the British Consul for North Formosa, referring to the great falling off in the exports, amounting to 33 % by weight, as compared with the exports in 1908, observes that it is chiefly due to competition both of the synthetic product and of Chinese camphor; in the case of the latter, in conjunction with the low price of silver. The decrease in the exports of Formosa camphor to Europe, both direct and via Hong-Kong, amounts, according to the British Consul to over 40 %.

According to a report by the German Consul in Kobe[3]) the prices (per 100 kin) which are paid to the producers of crude camphor and camphor oil by the Monopoly Bureaux in Old Japan were reduced on 5th March last to the following figures: —

	Crude camphor	Camphor oil
In Kobe	59 Yen	29.5 Yen
„ Nagasaki, Kumamoto Kagoshima and Fukuoka	57 „	28.5 „

[1]) Nachrichten f. Handel u. Industrie **1909**, No. 46, p. 3.
[2]) Diplomatic and Consular Reports, No. 4240, June 1909.
[3]) Nachrichten f. Handel u. Industrie **1909**, Nr. 47, S. 4.

As the German Consul in Colombo[1]) reports, the enthusiasm for camphor cultivation in Ceylon has considerably decreased in view of the lowness of the camphor prices. During 1907/8 only 200 acres of new plantations have been laid down. The exports were as follows: —

	cwts.	qrs.	lbs.	Value, Rupees
1907	8	3	17	4535
1908	14	3	20	3075

Kelway Bamber suggests that in order to expedite the process of distillation, the leaves and branches should be crushed between strong rollers.

A good many years ago[2]) the presence of cadinene in camphor oil fractions of high b. p. was discovered in our laboratories. Observations of the low sp. gr. of some camphor oil fractions of high boiling points have now induced us to investigate the subject afresh. For this purpose we employed a pale yellow, heavy camphor oil fraction possessing the following constants: b. p. 106 to 120° (7 mm.) $d_{15°}$ 0,9378, α_D + 11°, $n_{D20°}$ 1,50188. Any phenols present were removed by shaking with 5 % caustic soda liquor, and the remainder was fractionated. The b. p. now lay between 97 and 116° (5,5 to 6 mm.). As the b. p. rose the sp. gr. decreased from $d_{15°}$ 0,942 to $d_{15°}$ 0,905, while on the other hand the rotation increased from α_D + 4° 52′ to α_D + 16° 53′. No hydrate, nitrosite or nitrosate was obtained, but from the intermediate fractions we succeeded in isolating small quantities of a nitrosochloride, although the yield of this was too small to admit of further examination. By passing hydrochloric acid into the strongly cooled ethereal solution, we obtained an insignificant quantity of a readily crystallising chloride. In order to recover this chloride, the ether was evaporated, and the residue, after being stirred with alcohol, was placed in a freezing mixture for a few days. In the course of this process crystals separated out which, when recrystallised from alcohol, melted at 79 to 80°. This hydrochloride proved to be identical with the tri-hydrochloride of bisabolene, which (as we show on p. 64) is also a constituent of oil of lemon. When equal parts of the two tri-hydrochlorides were mixed, the m. p. was not reduced. The hydrocarbon was regenerated with sodium acetate and glacial acetic acid. B. p. 261 to 262° (752 mm.); $d_{15°}$ 0,8798; α_D ± 0; $n_{D20°}$ 1,48246. The tri-hydrochloride which was again obtained from this body melted at 79 to 80°.

Cadinene could not be detected in this fraction, and must therefore presumably be looked for in those with still higher boiling points.

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[1]) Ibid. **1909**, No. 45, page 3.
[2]) Bericht April **1889**, 9.

At the first general meeting of the Seventh Intern. Congress of Applied Chemistry, A. Haller[1]) referred to natural and artificial camphor. After describing the origin and mode of production of the natural product and giving statistics of exports and price-fluctuations, he pointed out that the increasing demand for manufacturing purposes, such as celluloid, smokeless powder, leather-substitutes, etc., taken in conjunction with the scarcity of natural camphor, was highly favourable to the development of the artificial camphor industry, which is based upon the conversion into camphor of the pinene of the various oils of turpentine. Haller divides the methods of preparing the artificial product into two groups; in one of which pinene is first converted into its hydrochloride, while in the other it is subjected directly to the action of organic acids. According to the author the comparison which is often drawn between the development of the synthesis of alizarin and indigo, and the camphor industry as regards the displacement of the natural products concerned, is in so far untenable that, whereas the cultivation of madder has ceased altogether, and that of indigo has been largely abandoned, the planting of camphor trees is making steady progress. Moreover, the raw material of synthetic camphor, i. e. oil of turpentine, is only available in limited quantities and at fluctuating prices. Hence, Haller regards the future of the artificial camphor industry as very uncertain.

We are nevertheless inclined to think that the foundations are already laid down on which afterwards, when times have become more favourable, this branch of industry may be reared to profitable development. The development of the artificial camphor industry may depend in the first place upon the relation between the prices of oil of turpentine and of camphor.

In view of the by no means inconsiderable quantities of synthetic camphor which have been brought to market up to the present time, the possibility of distinguishing the artificial from the natural product is a matter of great importance, especially in pharmaceutical practice. Racemic camphor, including, therefore, the synthetic article, has a different physiological action from the optically active forms to which Japanese camphor belongs[2]). A paper read by W. Lohmann[3]) before the German Pharmaceutical Society, dealing with the indications of difference between natural, artificial and synthetic camphor, may therefore be of interest. Lohmann associated himself in the main with the statements of Crane and Joyce[4]) to which we wish to

[1]) Chem. Ztg. **33** (1909), 621.
[2]) Comp. Report April **1908**, 176; November **1908**, 161; April **1909**, 113.
[3]) Berichte d. deutsch. pharm. Ges. **19** (1909), 222.
[4]) Comp. Report October **1907**, 27.

refer hereby. In order to determine the quantity of borneol which may be present he proposes to acetylate the sample in the familiar manner and then to saponify it. To determine the absence of chlorine from synthetic camphor, which is a matter of special importance where the article is intended for use in celluloid manufacture, Lohmann applied calcination with chlorine-free caustic lime. In the discussion ensuing, on the other hand, Stephan recommended Beilstein's copper oxide test, which for the particular purpose under review he regarded as more exact than the well-known combustion method, as it is said to be possible, by it, to detect so small a proportion as 0,02 % of chlorine.

With reference to the above statements we wish to observe that for the purpose for which it was devised, that is to say, for the detection of chlorine in bitter almond oil, the combustion test is much more suitable and gives much more trustworthy results, than does the copper oxide test.

According to E. Deussen [1]), the test of official spirit of camphor for its d-camphor content, as laid down in the German Pharmacopœia, ed. IV., is insufficient, because it is limited to the ascertainment of the specific gravity and a rough estimation of the camphor-content. The latter determination is made by diluting 10 g. of the spirit of camphor with 4,6 to 5,3 cc. water, after which it is said that the camphor will separate out. If less than the required proportion (10 %) is present, and assuming the spirit to be of the proper strength, no separation will take place until more than 5,3 cc. of water has been added. On the other hand, a preparation containing but little camphor in too highly diluted alcohol will not require more than 5,3 cc. water before turning cloudy, and may thus be able to pass as a preparation of the proper strength. Moreover, with the Pharmacopœia tests it is not possible to detect the presence of artificial, inactive camphor; on the contrary, this can only be discovered by determining the optical rotation of the substance. Deussen has found an average rotation, at 17° in a 10 cm.-tube, of $+3° 27'$. This constant is fairly certain, as the sp. rot. of pure Japanese camphor only varies very slightly from $[\alpha]_D + 44{,}22°$ (in 20 per cent. alcoholic solution). The camphor-content must be determined quantitatively by treating 5 g. of spirit of camphor with 20 g. solution of sulphate of ammonia and subsequently adding 30 g. of water or ice; the loss caused in the course of this manipulation by filtering and drying on a porous tile ranging from 4 to 6 %. The camphor which has separated out may then be treated further for camphoric acid, in order to identify its origin. For this purpose

[1]) Arch. der Pharm. **247** (1909), 307.

5 g. of camphor is placed in an acetylation-flask surmounted by a Liebig condenser and heated for 50 hours in the water bath with 24 cc. nitric acid ($d_{15°}$ 1,42) and 16 cc. water. The camphoric acid, which separates out in crusts, is recrystallised from water, converted into its sodium salt by means of soda, and again recovered from the latter with hydrochloric acid. Treated by this process, Japanese camphor yields d-camphoric acid, m. p. 187°, whereas artificial camphor gives an inactive acid, m. p. 204 to 205°. In conclusion the author recommends the incorporation into the next Edition of the German Pharmacopœia of his quantitative camphor-determination as well as the requirement therein of a test as to optical rotation.

Cananga Oil. This article has been available in plentiful quantities of exquisite quality, and it has therefore been possible further to reduce the prices somewhat in course of the summer.

Cananga oil has not been so cheap for years as it is now; hence no risk whatever would probably be incurred in placing considerable contracts.

Caraway Oil. The favourable prospects of which we were able to report in April have been realised. During the flowering period the weather was very suitable, and although owing to the subsequent damp weather this year's Dutch seed is rather dark in colour, we are nevertheless on the threshold of a crop which for quantity has not been equalled for years. During the last few months the prices have only been receding very slowly, as the demand has continued very brisk and the stocks of old seed have hardly been sufficient to answer the requirements.

According to official statistics the area under caraway cultivation in Holland during the past 5 years has been as follows: —

7158	hectares[1])	1909
4405	„	1908
4925	„	1907
4636	„	1906
4295	„	1905

divided as follows over the various districts: —

	1909		1908
Groningen	1898 hect.	against	922 hect.
Friesland	49 „	„	22 „
Utrecht	10 „	„	4 „
North Holland	2956 „	„	1874 „
South Holland	271 „	„	173 „
Zeeland	1127 „	„	736 „
Brabant	847 „	„	674 „
	7158 hect.	against	4405 hect.

[1]) 1 hectare equals about 2,5 acres.

The latest report by the Dutch Board of Agriculture dated 20th July asserts that everywhere the expectations of the yield of the crop are good. Only in South Holland and in the Western part of North Brabant a "fairly good" result is expected. In Zeeland the cultivations have suffered from heavy rains, and in North Brabant from night frosts during the flowering period.

The total yield is estimated at 30 to 35 bales per hectare, so that in the present year the important total quantity of about 200000 to 220000 bales may be expected, as compared with 140000 bales in the preceding year. The crop is late, and as the supplies are only being brought to market by degrees, the prices of first-class quality, such as is exclusively distilled by us, have been able to maintain themselves at about fl. 16.— per 50 kilos.

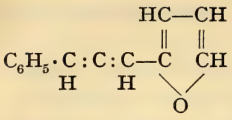
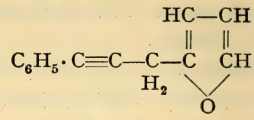
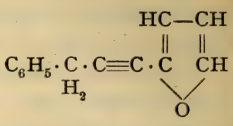
Thuringian und East Prussian seed, which is again offered this year from various quarters, is kept too high in price to utilise it for distilling purposes. With regard to Norwegian caraway nothing has yet been heard. We were able to reduce our quotations for caraway oil, carvol (carvone) and carvene as early as September last; but we will not let the occasion pass without again calling special attention to the excellence of our manufactures, as from various quarters we have met with competing distillates which, although of normal physical constants, possess by-odours rendering them entirely unsuitable for use in liqueur manufacture.

J. Henderson[1]) reports on a case of adulteration of caraway oil with castor oil. The sample under examination answered the requirements of the British Pharmacopœia, the sp. gr. being correct, viz., $d_{15,5°}$ 0,9119, from which a carvone content of 54% might be inferred. The optical rotatory power was + 69,7°. But, singularly enough, it did not give a clear solution with 10 vols. of 80 per cent. alcohol, as it should have done if the carvone content had been as high as was inferred. A carvone determination by means of sodium sulphite, in fact, showed that it only contained 29%, and after fractional distillation there remained a residue of 16% which was identified as castor oil. Henderson arrives at the conclusion that the British Pharmacopœia test for caraway oil is insufficient, inasmuch as the case under review shows that oils which, upon closer examination, prove to be heavily adulterated, are able to conform with its requirements.

Oil of Carline Thistle. The oil distilled from carline thistle (*Carlina acaulis* L., N. O. Compositæ) contains, according to the investigations of Semmler[2]) to which we have previously referred, as its chief

[1]) Pharmaceutical Journal **82** (1909), 610.
[2]) Berl. Berichte **39** (1906), 726; Report April **1906**, 15.

constituent an oxide-like body, carlina oxide, which the author holds to be phenyl-1-α-furyl-3-allene. Semmler[1]), in conjunction with Ascher is trying to throw further light on this oxide by endeavouring to arrive at a decision between the two isomeric formulæ

To attain this object he has tried to effect a synthesis of carlina oxide. Although this synthesis has not been successful, yet in the course of the experiments certain new bodies were discovered, among which we may here mention dihydro carlina oxide. By reducing fural acetophenone (phenyl-1-α-furyl-3-propene-2-one-1) which had previously been obtained by condensing acetophenone and furfurol, the principal product is obtained in the form of the corresponding saturated alcohol $C_{13}H_{14}O_2$, which possesses the following properties: b. p. 168 to 170° (12 mm.), $d\frac{20°}{4°}$ 1,10, n_D 1,55, mol. refr. found 58,89, calc. for $C_{13}H_{14}O_2$ 58,97. Analysis confirmed the formula $C_{13}H_{14}O_2$. From the optical data the authors conclude that the body represents phenyl-1-α-furyl-3-propanol-1, $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot C_4H_3O$[2]).

In order to identify this body more closely they prepared from it: the phenyl urethane (m. p. 95,5 to 96°), the acetic ester (b. p. 171 to 172° at 11 mm.; $d\frac{20°}{4°}$ 1,09; n_D 1,526); the ethylic ether (b. p. 145 to 147°, $d\frac{20°}{4°}$ 1,055; n_D 1,545); the chloride, phenyl-1-α-furyl-3-chloro-1-propane (b. p. 154° at 10 mm.; $d\frac{18°}{4°}$ 1,13; n_D 1,552). By heating this chloride from 3 to 5 hours in a tube, with an equal weight of melted sodium acetate and twice its weight of glacial acetic acid, to 170 to 180°, hydrochloric acid was given off. The product of reaction possessed the following constants: b. p. 146,5 to 147° (13 mm.), $d\frac{20°}{4°}$ 1,029, n_D 1,552. The analysis agreed for $C_{13}H_{12}O$. From the above it may be concluded that the splitting-off of hydrochloric acid had resulted in the formation of dihydro carlina oxide (phenyl-1-α-furyl-3-propene-1); the equation being as follows: —

$$\underset{\text{Phenyl-1-}\alpha\text{-furyl-3-chloro-1-propane}}{C_6H_5 \cdot CHCl \cdot CH_2 \cdot CH_2 \cdot C_4H_3O} - HCl = \underset{\text{Dihydro carlina oxide.}}{C_6H_5CH : CH \cdot CH_2 \cdot C_4H_3O}.$$

In its physical constants, dihydro carlina oxide occupied an intermediate place between carlina oxide and tetrahydro carlina oxide.

Cassia Oil. Since our last Report this article has become a little firmer, but on the whole it was possible to maintain the prices

[1]) Berl. Berichte **42** (1909), 2355.
[2]) For details see P. Ascher's Inaug. Dissert., Berlin 1909.

without change. All imports of oil of high percentage found ready buyers, and the quotations were kept above 3/6. If the consumption should show any considerable increase in the course of the present month, higher prices will rule.

Celery Oil. An oil from the herb and seed of the wild celery (*Ache des marais*) which had been distilled in the South of France and was sent to us from that country, was of a pale yellow colour and had a pronounced odour of celery. It possessed the following constants: $d_{15°}$ 0,8713, α_D + 58° 30′, $n_{D20°}$ 1,47715, acid no. 1,8, ester no. 41,5. No clear solutions could be obtained even with 95 per cent. alcohol, the reason of this being that the oil, which was distilled last year, had become considerably resinified in the meantime. After rectification with steam (in the course of which process a residue of 7,7 % remained) its properties had undergone considerable change: $d_{15°}$ 0,8541, α_D + 70° 55′, $n_{D20°}$ 1,47489. Soluble in 6 vols. and more of 90 per cent. alcohol with slight turbidity.

Chamomile Oil. As is well known, there are plants of which the different parts contain essential oils of different composition, although all the oils are formed in schizo-lysigene cells, and are therefore built up in a similar manner (as for instance in the case of *Citrus Aurantium*). In the chamomile flower, however, essential oil is formed in two entirely different parts, which differ from each other with regard to the oil cells. This fact has been taken by A. Jama[1]) as the starting point of a study on the essential oil of chamomile.

The hollow calyx contains, at the part where the leaves are attached, a wreath of collateral bundles of cells, and in front of the phloëm of these are schizogene structures containing a secretion. The fruit-whorl and the stem of the flower is provided with hairs which secernate oil. These hairs consist of two rows of cells, showing the characteristic type of the glands of the Compositæ. In both containers, owing to the position of the secerning cells, the oil is formed centrifugally.

Jama has distilled both oils separately. From 4 kilos pure flowers he obtained 14 g. oil = 0,35 % and from 1 kilo of pure calices 5,1 g. oil = 0,51 %. The oil from the flowers possessed the familiar deep-blue colour, while the oil from the calices was faintly green, and turned yellow in the course of a few days. At ordinary temperature both oils were viscous. Jama found them to possess the following constants: —

Flower-oil: $d_{15°}$ 0,954, α_D ± 0°, $n_{D21°}$ 1,363734, sap. no. 74,4.

Calyx-oil: $d_{15°}$ 0,949, α_D ± 0°, $n_{D21°}$ 1,363716, sap. no. 33,7.

Chamomile Oil, Roman. From England, which is the usual source of supply of this oil, it is reported that, as a result of the

[1]) Apotheker Ztg. **24** (1909), 585.

unfavourable weather, the crop is not of any importance. The prices have already advanced considerably in the course of the summer and will probably have to be raised still further because, at any rate for the present, it is hardly likely that other producing districts will count for anything.

Champaca Flower Oil. According to a paper by Bacon[1]), both varieties of the champaca flower, the white as well as the yellow, are found in the Philippine Islands. Experts there esteem the yellow kind above the white, and maintain that it has the finest odour of any flower in the archipelago. An attempt made by Bacon to obtain oil from the flowers by steam distillation was a failure: he obtained only a very small quantity of oil, and its odour did not much resemble that of the flowers. On the other hand, maceration of the flowers with paraffin oil (improperly termed *enfleurage* by Bacon), produced an oil of excellent and intense odour. The process employed was to allow the flowers to remain for 24 hours in the paraffin oil and then to treat them with absolute alcohol. The same paraffin oil was used again for macerating purposes nine times after the first. As the loss of paraffin oil was great, it is intended to use volatile solvents for further experiments in extraction of the flowers. The champaca tree can be raised easily from seed and bears as early as the third year. It is true that the yield of flowers is much less than that of the ylang-ylang tree, but this discrepancy is made good by the much greater value of the champaca flower extracts.

Chrysanthemum Oil. According to S. Keimatsu[2]), a yellowish brown oil obtained by distillation (of the flowers?) from *Chrysanthemum sinense* var. *japonicum*, locally known as "Rionō-Kiku" to the extent of 0,8 % of the material, contains i-camphor, of which body 40 g. were isolated by the freezing-out process from 250 g. oil. The camphor was identified by means of its oxime (m. p. 116 to 117°, inactive), paracamphoric acid (i-camphoric acid) m. p. 202°, and its β-bromo derivative (m. p. 61°). The oil which was left behind after the removal of the camphor still contained considerable quantities of i-camphor. This oil had the following constants: $d_{15°}$ 0,9394, $[\alpha]_D$ — 12° 4′, acid no. 0, ester no. 0. In the fraction with the lowest b. p. l-camphene could be detected and was identified by conversion into *iso*borneol.

Cinnamon Oil, Ceylon. In an exhaustive article Cayla[3]) treats of the cinnamon tree, especially from the point of view of its distribution and cultivation. He considers in particular Chinese cinnamon,

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[1]) Philippine Journ. of sc. **4** (1909), A, 131.
[2]) Journ. of the Pharm. Soc. of Japan **1909**, No. 326, 1.
[3]) Journ. d'Agriculture tropicale **9** (1909), 164.

which, as is well-known, is obtained from *Cinnamomum Cassia* Bl., and Ceylon cinnamon, the product of *C. zeylanicum* Nees. In the case of the first-named species, all parts of the tree yield an almost identical oil, containing from 75 to 90 % cinnamic aldehyde, but in that of the latter the oils differ according to the parts of the plant from which they are prepared; for instance, the oil from the bark and branches is characterised by its content of cinnamic aldehyde, that from the leaves by eugenol, and that from the root-bark by camphor.

Cayla distinguishes a third species in *Cinnamomum Loureirii* Nees[1]), which furnishes the cinnamon used in Japan. The root-bark of this oil appears to contain, besides cinnamic aldehyde, a terpene with a lavender-like odour. The oil, which is exported from Tonquin and Annam, is said to be derived from *C. Loureirii*. After dealing exhaustively with the preparation and adulteration of cassia oil by the Chinese, the author treats of the cultivation of the Ceylon cinnamon, and the manner in which oil is obtained from this tree, which has also been acclimatised in Java, India and the Seychelles islands. For the purpose of laying down a plantation, a site which is protected from the wind must be selected; the tree is propagated from cuttings, runners, or seed. Plants taken from nurseries and planted in the shade of *Erythrina* grow best. Where the soil is fertile the first crop can be gathered during the rainy season at the end of the second year. The bark is collected by cutting a circle round the trunk, drawing vertical incisions downwards, and stripping. The stripped tree dies, but from the stump from four to six shoots grow up, so that a fresh crop can be gathered every year. Among the diseases to which the cultivated trees are liable, Cayla mentions one which affects the leaves and is caused by a fungus (*Aecidium Cinnamomi*), and another which is manifested by the forming of gallnuts on the leaves[2]).

According to the experience which has been gained in cinnamon-growing in the Seychelles[3]), the trees should be stripped in the second or third week of the rainy season, but in these islands the cultivation is still in the experimental stage, and the exports, as yet, are quite small.

In Annam, on the other hand, *C. Loureirii* has long been grown. The trade in the product is in the hands of the Annamese and Chinese, who distinguish the following commercial brands of cinnamon, viz., *Que-kep,* from trees over 4 inches in diameter; *Que-kien,* from

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[1]) Comp. Report October **1904**, 96; October **1906**, 23; Gildemeister and Hoffmann, *The Volatile Oils*, p. 391.

[2]) D. Bois and C. Gerber (Compt. rend. **149** [1909], 405) have studied this disease. It is partly caused by the larvæ of a leaf-flea (*Psylla*, according to E. Green), and partly by *Eriophyes Boisi* Gerb.; in the first case the shape of the leaf is not affected, in the latter the leaves lose their shape.

[3]) Report April **1909**, 33.

smaller trees and from trees which have been prematurely stripped; and *Que-thanh,* from branches.

It would be possible to produce large quantities of good quality cinnamon in Further India, but it is not advisable to recommend the extension of cultivation, because heavy over-production is to be feared. Generally speaking, this industry is in the hands of the Natives, and this is the best way for securing the continuance of its profitableness. Europeans should limit themselves to the trade in the produce.

According to Bacon[1]), another species of *Cinnamomum*, viz., *C. mercadoi* Vid. occurs in many parts of the Philippines. The Tagal name for the tree is *calingag*. 25 kilos bark of such a tree from the district of Lamao, Prov. of Bataan, when ground, yielded 260 g. = 1,04 % of a pale yellow oil, with an odour resembling sassafras, and possessing the following constants: $d\frac{30°}{4°}$ 1,0461, $\alpha_{D\,30°}$ + 4°, $n_{D30°}$ 1,5270. Aldehydes could not be detected either with bisulphite or with phenylhydrazine. Fractionation *in vacuo* at 10 mm. gave the following results:

Fr. 1 (77 g.) b. p. 119 to 124°, $n_{D30°}$ 1,5333.
Fr. 2 (9,2 g.) b. p. 124 to 130°, $n_{D30°}$ 1,5320.
Residue 11,5 g. $n_{D30°}$ 1,5278.

After repeated distillation at ordinary temperature, the first fraction showed the following constants: b. p. 235 to 238° (760 mm.) $d\frac{30°}{4°}$ 1,0631, $\alpha_{D30°}$ + 0,9°, $n_{D30°}$ 1,5335. Oxidation by means of chromic acid resulted in piperonylic acid, m. p. 227°. Heating with alcoholic potash and subsequent oxidation with permanganate yielded piperonal. From this it would seem fair to infer that the oil of this species of *Cinnamomum* consists almost entirely of safrol.

Two other samples of bark from a not specially indicated *Cinnamomum* species from the Davao district, in the island of Mindanao, could not be examined more closely owing to the insufficiency of the material, but judging from the taste and odour this bark did not appear to be genuine cinnamon. The oil-yield was 1,1 %. According to the accounts of older travellers, *C. zeylanicum* Nees is said to occur in Mindanao; American planters likewise assert that the true cinnamon tree exists in the back-country of Davao, and that its bark is an article of trade in a small way among the natives. It is hoped that before long it will be possible to clear up this problem.

Citronella Oil. Since our April Report no alteration worthy of mention has taken place in the quotations for this article, and in spite of all the fairly evident attempts of the native traders to ad-

[1]) Philippine Journ. of sc. **4** (1909), **A**, 114.

vance the prices, these remain to-day at pretty much the same level as six months ago — that is to say, about 1/- c. i. f., for future delivery, with a weak tendency.

The exports from Ceylon up to the end of July 1909 (so far as is known) amounted to 982468 lbs., compared with

742911 lbs. in the corresponding period of 1908,
687140 „ „ „ „ „ „ 1907,
580832 „ „ „ „ „ „ 1906,

The increase by about 50000 lbs., in the exports, to which reference was already made in our April Report, has therefore grown by this time to 240000 lbs., which probably constitutes a record. There is no doubt that this heavy excess must be attributed to the new producing districts which have lately been opened up in the southern parts of Ceylon, their influence upon the exports in the course of the past few months having been unquestionable. The fact that in these circumstances prices were able to maintain themselves, as was the case during the past 3 or 4 months, appears to indicate a renewed increase in the consumption of citronella oil, for nothing is known of any heavy speculative stocks which might possibly depress the prices. In spite of this relatively ready absorption of the increased arrivals, signs are not wanting that prices will yield a little later on. Already the most recent quotations have again fallen below 1/-.

In the export statistics from Ceylon, England still continues to figure as the principal customer for citronella oil, but it must not be forgotten that important quantities of the exports which are entered under the heading "England" are destined for shipment, via London, to New York or Germany.

In a previous Report[1]) we referred at length to a paper by Stapf on the classification and the new nomenclature of the Andropogon grasses. Stapf divides these grasses into 3 groups, called respectively *Cymbopogon, Andropogon* and *Vetiveria.* Citronella grass (*Cymbopogon Nardus* Rendle) is included under the 10 species of the first-named genus, and of this grass it is stated, among other details, that it only occurs in the cultivated state, and that its mother-plant is probably Mana grass, *Cymbopogon confertiflorus* Stapf (*Andropogon Nardus* var. *nilagiricus* Hack.), which grows wild in Ceylon and is poor in oil. J. F. Jowitt[2]) opposes these views. His investigations show that, besides

[1]) Report April **1907**, 30.

[2]) Annals of the Royal Botanic Gardens, Peradeniya, vol. IV, part IV, December **1908**, p. 185. From a copy kindly sent to us.

Mana grass, genuine citronella grass *C. Nardus* Rendle, also grows wild in Ceylon. Hence the surmise expressed by Stapf and referred to above appears to him of doubtful correctness. *C. Nardus* Rendle, which occurs in a wild state, is identical with the so-called "old citronella grass" (Winter's grass, Maha Pengiri) and forms a species distinct from Mana grass. It is possible that a third variety, known as Lenabatu grass, has resulted from hybridisation of citronella and Mana grasses. In these circumstances Jowitt considers it advisable to designate the Maha Pengiri variety as a separate species under the name of *Cymbopogon Winterianus*. In this case the name *C. Nardus* Rendle should be applied only to the Lenabatu grass. We refer to the original article for further details showing the reasons adduced by Jowitt in support of his views. This article may also specially interest many readers, because in it Jowitt gives a detailed botanical description both of the Mana and Maha Pengiri grasses. It may suffice if we refer to the derivation of the word Maha Pangiri (Maha Pengiri). Maha means "large" and Pangiri indicates the oil vapour which occurs when orange or lemon peel is pressed.

Another publication by the same author[1]) relates to experiments made by him, at the instigation of the Agricultural Society of Ceylon, in the cultivation of Andropogon grasses in the Patanas (open plains) of Ceylon, at an elevation of 4500 ft. In these experiments he employed the different varieties of citronella grass (Mana, Mana Pengiri, and Lenabatu), also lemon-grass (*Cymbopogon flexuosus* Stapf and *C. citratns* Stapf), as well as palmarosa and vetiver (khus-khus) grass and *Cymbopogon polyneuros*. Owing to the change in climatic conditions due to the high altitude *C. citratus* was altogether a failure, and the greater part of the remaining grasses also flourished but poorly, the soil being insufficiently rich for the proper development of the plants. Better results were obtained after the use of natural and artificial manure, most of the grasses either requiring the application thereof before they showed any proper development, or the oil being improved both qualitatively as well as quantitatively by the manuring of the plants. The latter result, for instance, was observed by Jowitt in the case of Mana grass, which in the green state only contained traces, and after drying slightly larger proportions, of oil of an unpleasant odour. Artificial fertilizing caused a noticeable increase in the oil yield, and the oil moreover acquired a much improved odour, although one altogether differing from that of citronella oil.

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[1]) Oil-yielding grasses grown at Craig, Bandarawela, elevation 4500 ft. Circulars and Agricultural Journal of the Royal Botanic Gardens, Ceylon. Vol. IV, No. 14, December 1908, p. 109.

In regard to citronella oil the statement is of interest that Winter's assertion, according to which Maha Pengiri was brought to Ceylon from Malacca[1]), is due, by Winter's own showing, to his having confused citronella grass with lemon-grass. A letter from Winter's grandfather, written in 1850, further discloses the fact that the latter commenced the distillation of citronella grass in 1839. This industry quickly developed so enormously that about the year 1850 the annual sale of oil in London exceeded £ 3.000, the price being then 1/- per ounce.

With regard to the differences between Maha Pengiri and Lenabatu, Jowitt expresses the view that the two grasses differ not only in leaf, flower, and odour, but also in the peculiarity that the roots of Maha Pengiri are more on the surface, while Lenabatu is more deeply rooted. He therefore designates the two plants respectively as "surface feeder" and "deep feeder". For the distillation of the grasses Jowitt used a copper still of a capacity of 115 to 120 lbs., surmounted by a dome-shaped helm, the object of which was to avoid the passing-over of oxidation- and resinous products of high boiling-points. In order to prevent the singeing of the distilling material, the still was provided with a sieve-bottom, which was held in its place in a most primitive manner by placing it on two blocks of wood. Direct heat was applied, and the distillation was a so-called water distillation. The grass was reaped in the evening before it was distilled, and was placed whole in the still, as there was no advantage in cutting it up. For a full charge of grass, 30 gallons of water was added, but when the charge of grass was less, the addition of water was not proportionately smaller; for instance, for 50 lbs. of grass 25 gallons of water was used. Each charge requires 4 hours to distil, the water which passes over first of all being returned to the still. Several tables are added giving details of the oil-yield of the various grasses, and for these, as well as other details, we refer to the original paper.

We are now able to add a few details in completion of the references to the preparation of citronella oil in the Malay Peninsula which were made in our April Report of 1908[2]). These details are taken from a paper by B. J. Eaton[3]), Government Chemist of the Federated Malay States, dealing with a locally produced distillate. The oil under examination came from Perak, and in its general behaviour corresponded to Java oil. The colour was a pale yellow, the total geraniol content was 82,4 %, of which 27,7 was geraniol

[1]) Chemist and Druggist **52** (1898), 646. See also Report April **1907**, 32.
[2]) Report April **1908**, 35.
[3]) Agric. Bull. of the Straits and Fed. Malay States **1909**, no. 4, p. 142. According to Chemist and Druggist **75** (1909), 21.

and 54,7 % citronellal; $d_{15,5°}$ 0,8890; soluble in its own vol. and more of 80 per cent. alcohol.

From an article by A. W. G. Bagshawe[1]) we learn that the tsetse-fly (*Glossina palpalis*) which is so much feared as the medium by which sleeping sickness in conveyed, has a pronounced dislike of of citronella grass; hence an extension of the cultivation of this grass would afford an additional means of combating this dangerous insect. Seeing that the fly's aversion from the grass is probably entirely due to the essential oil present in citronella grass, it would perhaps be advisable to make experiments as to how far it would be possible to protect man and beast from the tsetse-fly by means of citronella oil.

Clove Oil. The report of the British Vice consul in Zanzibar contains the following tables completing the statistical data for 1908.

Exports of cloves in the years 1906 to 1908: —

	1906 cwts.	1907 cwts.	1908 cwts.	1906 £	1907 £	1908 £
United Kingdom .	23667	29455	20389	61042	74179	40005
British India . .	44610	56542	61312	118840	143077	121944
Netherlands . .	13801	8500	5003	37155	19687	9447
U. S. A. . . .	6410	9843	5841	15932	20404	12305
Germany . . .	34297	49367	29438	92840	118064	59119
France	5230	3741	8205	13822	8391	15050
Austria-Hungary .	1344	625	759	3522	1405	1456
Italy	1469	1688	538	3685	4103	926
Other countries .	4054	2870	2219	9798	6811	4708
Total	134882	162631	133704	356636	396121	264960

Deliveries during the last 14 years: —

	Zanzibar frasilah	Pemba frasilah	Total frasilah
1895	146397	391460	537857
1896	119787	237090	356877
1897	90676	250954	331630
1898	60363	308485	368848
1899	139320	344764	484084
1900	49180	248935	298115
1901	49977	294709	344686
1902	58438	235106	293544
1903	146308	172811	319119
1904	36550	387846	424396
1905	91448	274893	466341
1906	189198	209211	398409
1907	179137	460051	639188
1908	141850	299952	441802

[1]) Third Bulletin of the Sleeping Sickness Bureau. According to the Lancet of 6th March 1909.

Results of the last 13 clove harvests: —

	Zanzibar frasilah	Pemba frasilah	Total frasilah
1895/96 . . .	165 901	413 124	579025
1896/97 . . .	84 592	224 362	308 954
1897/98 . . .	44 941	150 703	196 644
1898/99 . . .	149 417	481 565	630 982
1899/1900 . .	59 741	206 640	266 381
1900/01 . . .	37 567	201 192	239 759
1901/02 . . .	43 626	321 599	365 225
1902/03 . . .	175 420	251 780	427 200
1903/04 . . .	28 369	96 792	125 162
1904/05 . . .	79 860	675 683	755 543
1905/06 . . .	181 536	109 931	291 467
1906/07 . . .	56 833	202 633	259 466
1907/08 . . .	213 667	541 998	755 665

The following explanatory notes are added to these tables: —

"In comparing the figures of the years under review it must be borne in mind that each of them is counted from July to July. As, however, the time when the cloves are gathered varies from year to year, the shipments in the corresponding periods often show divergencies, and this is also the case in the present instance. In the year under review (1907/08) the crop amounted to about 190000 bales (mats), of which 126000 bales were delivered before the end of 1907. In the year 1908 110000 bales were shipped, of which 46000 represented the arrivals in the first half of the year reported upon (1908/09). The harvest is going on while this is being written, but up to the present it is impossible even approximately to estimate its extent.

The decline in the value of the clove exports is due to the fact that the prices were low in comparison with those of the two preceding years and to the accumulation of stocks which has occurred in consequence, these stocks being held back for a rise. The average price per frasilah of 35 lbs. was this year 12/2 d. for Zanzibar and 11/4 d. for Pemba cloves, against 13/$7^1/_2$ d. and 12/9 d. in 1907. Throughout the year the clove market was very firm; it opened at 11/$6^3/_4$ d. for Zanzibar cloves (average price in January) and closed at 12/$1^1/_2$ d. (average price in December). The lowest monthly average was reached in August, viz., 11/2 d., the highest of 13/4 d. in September. Pemba cloves averaged $10^1/_4$ d. less.

At the end of 1908 the price of cloves in London was $5^5/_{16}$ d. per lb., against $4^7/_8$ d. at the end of 1907."

With regard to the approaching crop, we have before us a London report dated from the beginning of September, according to which it is estimated 130000 bales, although the bull-party, according to custom, talk of a much smaller output. In view of the fact that there is not likely to be any lack of the necessary labour in Zanzibar in the future — (the want of which is said to have frequently badly affected the harvests in previous years) — the above figure has probably not been placed too high, and if it should be confirmed, it is reasonable — in spite of all efforts of the bull clique — to count upon lower prices. That a receding movement is in prospect (it is stated) is already clear from the fact that the unsold residue brought over from last

year's crop is said to amount to not less than 100000 bales in Holland, London, and New York only, so that, including the new crop, over 230000 bales are available. Even calculating upon 200000 bales only, this quantity would be more than sufficient for the normal requirements of one year. Hence, if the party interested in the rise should be unable to drive the price upwards, the market during the coming season will probably, and with good reason, be in favour of the consumers.

We reproduce this report under reserve, for pessimistic information from Zanzibar dated at the end of July is also at hand, in which a considerable shortage in the crop of 1909—1910 is forecasted.

According to a newspaper article, the intention exists of introducing the cultivation of cloves on the palm island of Mafia, which belongs to Germany and is situated south of Zanzibar[1]).

In the course of the period unter review the observation has been made again in London and in Hamburg that not only wholesale dealings in clove oil, but even quite small contracts, have been concluded at prices at which it is impossible for the manufacturers to have made any profit whatsoever. Both these centres appear to have made it their business to ruin the trade in clove oil by senseless competition.

Copaiba Balsam Oil, African. H. von Soden[2]) has published particulars of an investigation into the composition of an oil from African balsam. By passing hydrochloric acid into the ethereal solution he obtained from the oil (constants: d 0,920, $\alpha_D + 16° 50'$, ester no. 5,6, ester no. after acetyl. 10) a hydrochloride, m. p. 116 to 119° ($\alpha_D - 3°$ in 10 per cent. benzene solution). The hydrocarbon regenerated thereform had the following constants: b. p. 274,5 to 276° (743 mm.), d 0,928, $\alpha_D - 94°$. These properties agree with those of l-cadinene. It was not possible to arrive at a conclusion as to the particular sesquiterpene which occurs in the oil. Apparently, however, the conditions are somewhat similar to those which prevail in West Indian sandalwood oil, of which Deussen converted the dextrorotatory sesquiterpene into l-cadinene by way of the hydrochloride[3]).

In our Report of October 1908[4]) we gave the constants of an African Copaiba balsam and of the essential oil prepared therefrom. The oil ($d_{15°}$ 0,9215, $\alpha_D + 22° 26'$, acid no. 2,2, ester no. 0) has been more closely examined in our laboratories, but we have abstained from publishing anything about it because we knew that it was the intention of Dr. Deussen, of Leipzig, to investigate the separate con-

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[1]) See Report November **1908**, 46.
[2]) Chem. Ztg. **33** (1909), 428.
[3]) Arch. der Pharm. **238** (1900), 149.
[4]) Report October **1908**, 48.

stituents of the oil. The results of our examination agree wit those obtained by von Soden. 90 % of the oil had a b. p. of 267 to 276°; *in vacuo* it distilled between 118 and 125° (5,5 to 6 mm.) By introducing hydrochloric acid into the ethereal solution we obtained 37,5 % of a hydrochloride, crystallising in long needles, m. p. 117 to 118° ($[\alpha]_D$ — 37° 27′ in a 5,022 per cent. chloroform solution). The hydrocarbon, recovered by means of sodium ethylate, had m. p. 271 to 273° ($[\alpha]_D$ — 105° 30′). With hydrochloric acid, the hydrochloride, m. p. 117 to 118° ($[\alpha]_D$ — 36° 48′ in a 4,73 per cent. chloroform solution), was again obtained. Further investigation must show whether d-cadinene occurs in African copaiba balsam oil, or whether the dextrorotatory sesquiterpene is only converted into a derivative of l-cadinene by the action of the hydrochloric acid.

Coriander Oil will no doubt become scarce and dear, for owing to the low prices which have ruled during the last year and which did not cover the cost of growing to the farmers, the cultivation both in Russia and Moravia has been considerably reduced. In Hungary, it appears, coriander is not being grown at all this year. With regard to Russian coriander, we hear nothing except that a fair average crop is expected.

Of the constituents of coriander oil, only d-pinene and d-linalool have been known up to the present. Linalool was the principal subject of papers by Kawalier[1]), Grosser[2]), Semmler[3]), and Barbier[4]). The presence of pinene was first shown in our laboratory in 1892[5]). Subjoined we present the results of a fresh examination of coriander oil which has been carried out by us[6]).

The oil, distilled by ourselves from ripe coriander seed, possessed the following constants: — $d_{15°}$ 0,8735, α_D + 10° 24′, $n_{D\,20°}$ 1,46387, ester no. 20,22.

The determination of free alcohol (calculated for $C_{10}H_{18}O$) gave by the usual acetylation-method 49,65 %; by the Boulez process, as modified by us[7]) 67,5 %. An experiment of warming the dry oil in toluene solution with sodium and estimating the alcohol-content from the quantity of sodium consumed, gave 75 %. By careful fractionation

[1]) Liebigs Annalen **84** (1852), 351.
[2]) Berl. Berichte **14** (1881), 2485.
[3]) Berl. Berichte **24** (1891), 206.
[4]) Compt. rend. **116** (1893), 1460.
[5]) Report April **1892**, 22.
[6]) Detailed particulars are found in the Jubilee Publication issued in connection with the Wallach Celebrations at Göttingen (Vandenhoek & Ruprecht, 1909, p. 654), the paper in question being that of H. Walbaum and W. Müller: Zur Kenntnis der Bestandteile des Corianderöls.
[7]) Report April **1907**, 120.

on a commercial scale, about 70% d-linalool was obtained. It may therefore be considered that the linalool content of coriander oil is from 60 to 70%.

In the hydrocarbon fractions, amounting to about 20% of the oil, the following bodies were found present: i-*α*-pinene, identified by the nitrolbenzylamine, m. p. 123 to 124°, and i-pinonic acid, m. p. 104 to 105°; d-*α*-pinene, identified by d-pinonic acid, m. p. 68,5 to 70° ($[\alpha]_D$ + 89,40°), *β*-pinene, identified by oxidation with permanganate solution into nopinic acid, m. p. 125 to 127°. Furthermore we isolated p-cymene showing the following constants: $d_{15°}$ 0,8601, α_D ± 0°, $n_{D\,20°}$ 1,48565. When oxidised with permanganate, the cymol yielded p-hydroxi-*iso* propylbenzoic acid, m. p. 155 to 156°. Dipentene, which only occurs in the oil in very small proportions, could be identified through the tetrabromide, m. p. 123 to 124°. There were also indications of the occurrence of terpinolene and phellandrene, but they were insufficient to afford absolute certainty of the presence of these terpenes. A considerable part of the hydrocarbon fractions consisted of terpinene, including *α*- as well as *γ*-terpinene. Treatment with nitrous acid of the fractions boiling at 179 to 180° resulted in the formation of terpinene nitrosite, m. p. 154 to 155°. With hydrochloric acid gas the same fraction yielded a large proportion of terpinene dihydrochloride, m. p. 51 to 52°. The dihydrobromide melted at 58,5 to 59,5°. The hydrochloride, when treated with alkali by Wallach's method[1]), was readily converted into terpinenol. When the terpinene fractions were oxidised with diluted solution of permanganate of potassium, the erythritol, m. p. 235 to 236° was formed (which, according to Wallach's researches[2]) is derived from *γ*-terpinene) and likewise inactive *α*, *α'*-dihydroxy-*α*, *α'*-methyl *iso*propyladipic acid, m. p. 189°. This acid is a derivative of *α*-terpinene. It was thus evident that both forms of terpinene occur in the natural state. The presence of *α*-terpinene can readily be shown by means of the nitrosite test, and in some cases this body has already actually been discovered in essential oils, but until the more recent researches of Wallach the conditions of isomerism of this terpene were by no means clear. These researches, however, have made it possible to recognize the various terpinenes in mixtures and to identify them positively.

In the portions of coriander oil of which the boiling points lie above that of linalool, higher aliphatic aldehydes were found, chiefly decylic aldehyde, also geraniol, borneol and the acetic esters of these alcohols. The decylic aldehyde was identified more clearly by conversion into decylic acid and into its semicarbazone, m. p. 102°. In

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[1]) Liebig's Annalen **350** (1906), 155; Report April **1907**, 135.
[2]) Liebig's Annalen **362** (1908), 296; Report October **1908**, 175.

addition to decylic aldehyde, other easily changeable aldehydes appear to be present. The geraniol, obtained in the pure form by means of the calcium chloride compound, showed the constants which pertain to this alcohol: b. p. 231 to 232°, $d_{15°}$ 0,881, $\alpha_D \pm 0$. It yielded a diphenyl urethane, m. p. 80 to 81°. The borneol which was isolated was faintly lævorotatory; it crystallised from petroleum ether in hexagonal tables, m. p. 204°, and upon oxidation it yielded camphor, of which the oxime melted at 118°. In the saponification liquor which had been used for decomposing the ester-fractions, acetic acid and a little decylic acid were found present.

To sum up: the following bodies are now known as constituents of coriander oil, viz.,

d-α-pinene, i-α-pinene, β-pinene, phellandrene(?), cymene, dipentene, α-terpinene, γ-terpinene, terpinolene(?), n-decylic aldehyde, d-linalool, geraniol, l-borneol and acetic esters of these alcohols.

Cubeb Oil is very firm, cubebs being extraordinarily scarce and dear. We have repeatedly been compelled to advance the prices of our distillate.

Cumin Oil. The arrivals of the present season's seed, which have been so ardently expected, are now to hand, so that for the present there is again a supply of this oil, and we have been able to lower our prices in consequence.

Investigations into the constitution of cumin oil[1]) (*Cuminum Cyminum* L., N. O. Umbelliferæ) were begun as far back as the year 1841, and led to the result that cuminic aldehyde was found to be the principal constituent of the oil. In addition to the aldehyde, the oil is said to contain cymene and a terpene $C_{10}H_{16}$, called by Wolpian hydrocuminene.

The oil examined by us possessed the following constants: b.p. 165 to 280 (754 mm.), $d_{15°}$ 0,921, α_D + 4°20′, $n_{D20°}$ 1,50784. The hydrocarbons were separated from the fractions with higher boiling points by fractionation *in vacuo*. The fractions possessing a b. p. of over 80° (10 mm.) were shaken up with bisulphite, only small portions being left unaffected by this reagent. The examination, therefore, fell under the following heads: —

I. The hydrocarbon fraction.
II. The products reacting with bisulphite.
III. The portions not reacting with bisulphite.

I. The Hydrocarbons.

The hydrocarbons were again fractionated several times at ordinary pressure. As the b. p. rose, the rotation fell considerably; for

[1]) Gildemeister and Hoffmann, *The Volatile Oils*, p. 545 ff.

whereas the fraction boiling at 168 to 169° showed $\alpha_D + 14°40'$, that boiling at 178° showed only $\alpha_D + 0°35'$. Warren, Beilstein and Kupfer, as well as Wolpian, have isolated from cumin oil a hydrocarbon, of which the b. p. is given as 156° and as 157 to 158°, and to which Wolpian gave the name of hydrocuminene. After repeated fractionation we succeeded in obtaining from $2^1/_2$ kilos hydrocarbon 11 g of a body with b. p. 158 to 168° and an odour of pinene. Treated with nitrosylchloride a very small quantity of a nitrosochloride was obtained, of which the benzylamine-combination melted at 120 to 123°. The presence of α-pinene could be more readily proved by oxidation into active d-pinonic acid. The acid melted at 68 to 69° and was identical with d-pinonic acid from Greek oil of turpentine. It follows that the oil contains i- and d-α-pinene.

The fractions with higher b. p. contained, besides p-cymene, small quantities of terpene hydrocarbons. p-Cymene was identified in the familiar manner by oxidising with permanganate (hydroxy-*iso*propyl benzoic acid, m. p. 155 to 156°). When the cymene fraction was oxidised it yielded a small proportion of sodium nopinate. The free nopinic acid had m. p. 125 to 126° and was lævorotatory. On oxidation with permanganate it yielded nopinone, of which the semicarbazone melted at 187 to 188°, thus proving the presence of β-pinene. Wolpian, who had isolated considerable proportions of hydrocuminene from the oil, has probably had to deal with a sample which was adulterated with turpentine oil, and his hydrocuminene was certainly only a mixture of α-pinene, β-pinene, and p-cymene.

Although it was just the fraction boiling at 178° which showed the smallest rotation ($\alpha_D + 0°35'$), it yet absorbed about 10% of bromine. With hydrochloric acid it yielded a solid dihydrochloride, m. p. 48°, which, when mixed with dipentene dihydrochloride suffered no reduction of the m. p. From the same fraction a nitrosochloride was also obtained, but this only appeared in very small quantities and only separated out in the solid form upon the addition of water, alcohol and ether. These facts in any case point to the presence of dipentene.

The presence of terpinene could not be proved, neither from the nitrosite, nor from the dihydrochloride of m. p. 52°, or the products of oxidation. No fraction gave the nitrite reaction, and a considerable phellandrene content is therefore out of the question. The results of the oxidation with permanganate indicate a high probability of the presence of β-phellandrene, which proves that when small quantities of phellandrene are present, identification by the nitrite reaction is very often a failure. This also agrees with our observations in the case of other oils. 200 g. of the fraction, b. p. 173°, were oxidised

with a 1 per cent. permanganate solution. The hydrocarbon which hat not been attacked consisted almost entirely of p-cymene. The oxidation liquors were evaporated and extracted with chloroform. The glycol which was isolated was a viscous oil which could not be brought to congealing. With dilute sulphuric acid we obtained a body of a pronounced odour of cumin, of which the semicarbazone melted at 205 to 208°. The parts which were not attacked by the semicarbazide probably represented a hydrated cuminic alcohol, which was converted by oxidising with chromic acid into cuminic acid, m. p. 113 to 115°. The aldehyde which was reconstituted from the semicarbazone was also converted into the same acid. Hence, these fractions must contain a hydrocarbon with a methene-group connected to the nucleus, for only such a body is able to form, when oxidised, a glycol which when water is eliminated therefrom is converted into an aldehyde and an alcohol of the cumin series. In addition to this glycol there was formed a mixture of oily acids from which, however, only *iso*butyric acid could be isolated. The b. p. of this was 157 to 159°; its calcium salt dissolved more readily in cold than in hot water. From what particular hydrocarbon these oxidation products were derived could not be exactly determined, but it may be safely assumed that they indicate the presence of β-phellandrene; for β-terpinene, which would yield similar products, could not be detected by other methods.

In order to settle also the question as to what particular hydrocarbons are the source of the liquid chlorides which are formed in ample quantities in the course of the preparation of the chlorides, these liquid chlorides were subjected to closer examination. The bulk of them boiled between 83 and 85° (5 mm.).

0,1554 g. gave 0,1901 g. Ag Cl, corresponding to a content of 30,24 % Cl. Calculated for $C_{10}H_{18}Cl_2$, 33,97 % Cl; for $C_{10}H_{17}Cl$, 20,58 %. The values agree to some extent for dihydrochlorides.

22 g. of the liquid dihydrochlorides were shaken up for 4 hours at 50° with 25 g. potassium hydroxide and 1250 ccm. water and this operation was repeated until the oil ceased to give a chlorine reaction. The volatile constituents were then driven off by steam distillation. In the residue only *cis*-terpin hydrate, m. p. 117 to 118°, could be detected. The portions which volatilised with steam contained dipentene (tetrabromide, m. p. 123 to 125°) and α-terpineol, m. p. 33 to 34°. The alcohol which had not solidified, when treated with hydrochloric acid, yielded dipentene dihydrochloride, m. p. 48 to 49°, and when oxidised, a glycerin which was converted into the ketolactone, m. p. 60 to 63°, by chromic acid. This alcohol, therefore, also consisted of α-terpineol.

It follows that the hydrocarbon-fractions consist for the greater part of p-cymene; in addition to which there are present (but only in small quantities) d- and i-α-pinene, β-pinene, β-phellandrene and dipentene.

II. The Aldehydes.

The bisulphite-combination, after being purified by washing with alcohol and ether, was decomposed by boiling it with soda solution and then distilled by steam. Its constants were as follows: b. p. 97 to 99° (7 mm.) $d_{15°}$ 0,9731, α_D +0° 3′. When oxidised with chromic acid the aldehyde was converted into cuminic acid, m. p. 113 to 114°. The m. p. of the semicarbazone was 210 to 211°, of the oxime, 55 to 57°[1]). Cuminic aldehyde (cuminol) which has long been known as forming the principal constituent of oil of cumin, is here present in a state of great purity. It caused some surprise, however, to find the first fraction of the aldehyde showing a slight rotation to the right (α_D +1° 13′), but oxidation always gave only cuminic acid. In the course of the fractionated crystallisation of the semicarbazone we succeeded in obtaining, in addition to cuminic aldehyde, semicarbazone, crystallising in pretty flakelets, (m. p. 210 to 211°), another body, m. p. 200 to 201°, crystallising in thin prisms. This latter semicarbazone was not found in the other fractions. Further examination failed to confirm the surmise that the two semicarbazones of cuminic aldehyde contained *cis*- and *trans*-modifications. When oxidised with chromic acid, the aldehyde forming the basis of the semicarbazone of the m. p. 200 to 201° was also converted into cuminic acid. The oxime of the aldehyde had a m. p. 72 to 76° (impure). It is therefore probable that, in addition to the cuminic aldehyde, there is present, in small proportions, a hydrogenated cuminic aldehyde. We intend in a future contribution to give details of the further examination of this body.

III. Cuminic alcohol.

The constituents of the oil which possessed higher boiling points and did not react with bisulphite also had the typical cuminol odour. These were repeatedly shaken with semicarbazide solution. 12 kilos cumin oil yielded altogether about 20 g. Ester no after acetyl. 211. It was found impossible to prepare any characteristic derivatives. When oxidised with permanganate, cuminic acid, m. p. 112 to 113°, was formed. As the cuminic aldehyde itself had been carefully removed from the oil, the only possible conclusion points to cuminic alcohol. Besides

[1]) Wallach (Liebig's Annalen **340** [1905], 6) gives the m. p. as 58 to 59°, whereas Westenberger (Berl. Berichte **16** [1893], 2994) has found it to be 52°.

this cuminic alcohol there occurs in the oil a small quantity of a body melting at 90 to 107° (3 mm.). This part of the oil can only be examined in detail when larger quantities are available. We shall continue the examination as soon as an opportunity presents itself.

Curcuma Oil. Since our last Report on curcuma oil, in which we discussed the results of an examination of the oil which was carried out by H. Rupe[1]), this investigator, in conjunction with E. Luksch and A. Steinbach[2]), has published a detailed communication on the subject, from which we quote the following in completion of our previous notes: —

The ketone $C_{13}H_{18}O$ which is formed when curcuma oil is boiled with alkali liquor (the authors call this ketone curcumone) is a colourless, not readily liquefying oil, of a pungent odour reminding of ginger. It possesses the following constants: — b. p. 119 to 122° (8 to 11 mm.), $d_{20°}$ 0,9566, $[\alpha]_{D\,20°}$ + 80,55°, n_D 1,50526, mol. refr. found 58,98, calculated 58,93. With the exception of certain slight differences in the melting points, the derivatives have the same properties as those observed on the previous occasion: phenylhydrazone m. p. 92°; benzylidene curcumone, m. p. 106; piperonal-curcumone, m. p. 113°. The condensation-product with anisic aldehyde, prepared on the present occasion, is a new derivative. It consisted of lustrous white flaky crystals, melting at 77 to 78°.

When curcuma oil is treated with acids it is also converted into curcumone, but this method is not a suitable one, because the yield is very small. Up to the present, in spite of many efforts, the authors have not succeeded in identifying the alcoholic constituent of the oil.

Cypress Oil. We are just ready with distilling a fairly considerable parcel of cypress leaves, so that we are again in a position to supply fresh oil for the coming winter season, when, as usual, more or less severe epidemics of whooping cough may be expected. The excellent medicinal effect of cypress oil is so generally known that it is hardly necessary to refer to it here, but we wish to sound a special warning against the many cheap qualities which are on the market, as they are frequently manufactured of doubtful material and their medicinal action may therefore not be satisfactory. Numerous samples of cypress oil of French origin in particular, when examined in our laboratory, have been found to be of inferior quality.

Dr. H. Winterseel[3]) has published a communication on the pharmacodynamics of this oil which deals with its action upon various warm

[1]) Berl. Berichte **40** (1907), 4909; Report April **1908**, 36.
[2]) Berl. Berichte **42** (1909), 2515.
[3]) Das Cypressenöl. Inaug. Dissert., med. Fac., Bonn, 1908.

and cold-blooded animals, bacteria, blood, albumen, and milk, as well as upon human beings. He found that the effects of the oil were those common to most essential oils, viz., in the case of animals: indications of paralysis, hemolysis, arrestation of bacterial development, precipitation of albumen, acidification of the milk, etc. But all these symptoms were only observed in slight degree, and only when large doses were administered. Special comparative experiments on warm and cold-blooded animals, both normal specimens and others whose reflex-excitations had been increased by the administration of spastic poisons, such as brucine, showed that cypress oil, in both experimental series, causes a reduction, and in certain circumstances a cessation, both of the normal and of the pathologically increased reflex-excitation, and that it allays attacks of paralysis. These effects supplied the author with a reason for the favourable action of inhalation of cypress oil vapour in cases of infantile whooping cough, such as had been observed by him, and, in like manner, at an earlier date by Soltmann [1]). Winterseel reports altogether on 14 cases of pertussis of children at ages varying from 5 weeks to 10 years. In all these cases relief was obtained when cypress oil vapour was inhaled for a sufficiently long time. The attacks diminished both in violence and frequency; bleeding from the nose and vomiting were reduced, and the patients' appetite and weight increased. In a few cases the frequency of the attacks was reduced by more that one-half within a few days of the commencement of the cypress oil treatment, and after from 2 to 4 weeks they, only occurred sporadically. When the use of the oil was temporarily suspended the frequency of the attacks of coughing increased again, exactly as was observed by Soltmann at the time. With regard to the excellent services rendered by the oil in whooping-cough, Winterseel associates himself entirely with the statements of Soltmann, which he quotes textually. Similar good results have also been observed in other quarters.

Elemi Oil, Manila. In amplification of previous notes [2]) we take from a lengthy paper by Bacon [3]) in the first place the reference to the original publication, in which Merrill finally and definitely recognised *Canarium luzonicum* (Miq.) A. Gray as the plant from which the Philippine elemi resin is derived [4]). In opposition to Tschirch, who distinguished three varieties of Manila elemi, viz., hard, soft, and Tacamahac elemi, Bacon declares that Manila elemi in the fresh state, as taken from the tree, is always soft and only becomes

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[1]) Therapie der Gegenw., March 1904; Report April **1904**, 36; October **1904**, 22.
[2]) Report April **1907**, 41; October **1907**, 37.
[3]) Philippine Journ. of Sc. 4 (1909), A, 93.
[4]) Gov. Lab. Pub. **29** (1905), 51.

hard after prolonged exposure to air and sunlight. After giving some details as to the manner in which the Chinese conduct the trade in elemi, Bacon turns to the mode of collecting the gum. He states that it flows in the trunk of the tree chiefly when the tree is beginning to develop new leaves, and that in the principal place of production, viz., Atimonan, in the district of Tayabas, this takes place about January and June. During the rest of the year the tree is shedding its leaves and yields no resin. For the purpose of collecting the balsam the natives make incisions in the tree with tools known as *bolos*. The resin then exudes from the cuts and collects on the bark, from which it is removed once every few days, before it has grown dirty or hard. Bacon concludes from his own examinations that healthy, full-grown trees are capable of yielding annually 4 or 5 kilos of gum. One large tree produced as much as 22 kilos in 2 months. The production of essential oil from the various varieties of elemi, of different origin but of the same botanical derivation, was carried out by distilling the fresh gum *in vacuo*, separating the resultant oil from the water, drying with chloride of calcium, and again distilling *in vacuo*, in which process only the terpene fraction was considered, which was again distilled by Bacon under ordinary pressure. Of 62 samples, taken from different trees at Calaoag, in the district Tabayas, only two contained d-limonene: b. p. 174 to 176° and 175 to 176,5°, α_D + 89,0 and + 96°, respectively. The other samples contained phellandrene; their boiling points varied from 168 to 179° and their rotation lay between + 134,5 and — 60,6°. In dealing with this matter, Bacon describes as "phellandrene" a terpene which yields a crystalline nitrite, with a m. p. not exceeding 121°. The separate phellandrenes were mixed as follows: — first the 6 lævorotatory samples ($\alpha_{D30°}$ — 30,3 to — 60,6°), next, according to the elevation of the b. p., the 17 samples with low b. p. (168 to 173°), then the 30 samples with intermediate b. p. (up to 175°), and finally the five samples with the highest b. p. (175 to 179°). Out of nine elemi oil terpenes from samples of resin taken at Gumaca, in the Tayabas district, six contained d-limonene (α_D + 111,8 to + 117,9°), two are alleged to have contained β-phellandrene (b. p. 165 to 169° and 166 to 169°, α_D + 92,2° and + 90,7° respectively) and one contained α-phellandrene (b. p. 173 to 175°, α_D + 107,6°). As Bacon appears to describe these two terpenes as "β-phellandrene" simply because of their low b. p., and as, moreover, he obtained from a terpene which he regarded as pure β-phellandrene a nitrite of m. p. 121° (according to Wallach the two varieties of β-phellandrene nitrite melt at 102° and 97 to 98° respectively) while furthermore, oxidation of the substance with permanganate yielded the aldehyde phellandral, it would seem that more convincing proofs are needed before the presence of the terpene referred to can be regarded as

positively established. Bacon only carried out oxidation-tests with the object of quantitatively determining α- and β-phellandrene side by side in the separate oils, in which attempt he did not succeed. It is said that the elemi terpenes contain still a third phellandrene with a higher boiling point, and possessing the following constants: b. p. 175 to 178° at 760 mm., $d\frac{30°}{4°}$ 0,8375, $\alpha_{D30°}$ (+?) 82,4°, $n_{D30°}$ 1,4685, which also yields a nitrite melting at 121°. Other elemi samples from Culion and from the island of Mindanao gave terpene fractions containing hardly anything except pinene, as was shown by the fact that, when treated with hydrogen chloride, a hydrochloride melting at 125° was obtained. Altogether 90 % of all the elemi samples of various origin which Bacon examined were found to contain phellandrene.

So far as the technical details of the collection of elemi are concerned, it is stated that the best means of cleaning the crude, and often dark and dirty gum, consists in dissolving it in benzene and in freeing the filtered solution from benzene by distillation, as a result of which a pale product of the same scaly structure as elemi remains behind. The residue of resin which is left in the preparation of the oil appears to be suitable for the preparation of lacquers and varnishes, and further experiments are being carried out in this direction. By dry distillation of this residue an apparently valuable resin oil was also obtained.

Further researches by Bacon had for their object the investigation of the properties of the hydrocarbons obtained from elemi oil, viz., limonene and phellandrene. In the case of the latter the remarkable circumstance was observed that the optical rotation diminished considerably under the influence of sunlight; much more so, in fact, than under that of heat. An α-phellandrene, originally recording α_D + 134,5°, showed only + 132° after two hours' exposure to sunlight, after 8 hours more only + 124,7°. Another sample which rotated in the original state + 125,5°, showed only + 101,5° after a week's exposure. A "β-phellandrene", originally α_D + 76,7°, became noticeably more viscous in the course of a week and gave only + 32,1°. On the other hand, in the same period of time, the rotation of limonene only diminished from + 96° to + 94,9°; the change, therefore, being almost negligible. Other investigations related to the conversion of limonene and phellandrene monohydrochloride and -bromide with magnesium and benzaldehyde, in the manner already described[1]). As noticed at the time, the reaction proceeded abnormally, inasmuch as, when the products of reaction were treated with water, the corresponding dihydroterpenes were formed, along with benzaldehyde and a little benzoin. The same conversion of limonene dihydrochloride produced tetrahydrolimonene.

[1]) Philippine Journ. of sc. **3** (1908), A, 49; Report November **1908**, 173.

Essential Oils, Sicilian and Calabrian.

Our experienced informant, Mr. Eduardo Jacob, of Catania, writes as follows: —

Before proceeding to a discussion of the different varieties of essential oils, it is necessary to point out that in consequence of the earthquake it has become exceedingly difficult to form a judgment of the statistical position of our essential oil market. Formerly, when by far the greater part of the trade in essences was centred in Messina, and when compared with the Messina shipments those from other Sicilian ports and from Reggio were of more or less secondary importance, it was possible to obtain continuous and exact statistics concerning the exports, but at the present time this is still altogether impossible. In my April report I have already referred to the probability that after the earthquake the trade in essences would be split up, and this surmise has been realised, for whereas formerly nearly three-fourths of the output were shipped via Messina and Reggio, the exports via Catania and Palermo have considerably increased since the catastrophic earthquake. A new organisation is required for the purpose of procuring details as to the shipments from the various ports, and it has as yet been impossible to form such an organisation, partly owing to the difficulties encountered in the Sicilian Custom houses, and partly because in various towns no statistics concerning essences are being kept.

But, although exact figures are not available, the reports which have been received enable us to conclude that the exports during the past half-year have not fallen behind those of the corresponding period of 1908. Indeed, it may even be assumed that, especially as regards oils of lemon and orange, they have been larger. The impending new Customs Tariff in the U. S. A. has induced many of the American import houses, at a time when ordinarily the requirements of American buyers are slight, to lay in considerable stocks of both these oils before any duties which might be adopted should come into force. Hence, during the months from April to June, an extraordinarily brisk exportation took place to the United States, which is now the principal place of outlet of Messina essences. Later, in the course of the debates on the Tariff, the conviction gained ground that oil of lemon would remain on the free list, and the demand then slackened off again. On the other hand, large quantities of orange oil were hurriedly thrown across the Atlantic, so that they might arrive before the new duty came into force. With regard to the separate varieties of essential oils, the following may be noted: —

Bergamot Oil. When once the panic which followed the earthquake, and as a result of which the prices of this article abroad had

been driven to record-figures (it is said that the price of 100 marks has been exceeded several times), had subsided, and when it became evident that notwithstanding the great loss of human life and of the plant required for the production of the oil it was possible to resume manufacturing (which had hardly commenced at the time when the earthquake occurred), the prices abroad again fell to a point in accord with the quotations prevailing here. Nevertheless, the prices which ruled in the district where bergamot oil is produced were very considerably higher than they had been for many years past, and apart from local conditions this tendency was stimulated by the exceedingly brisk demand on the part of foreign buyers, and especially by the appearance on the spot of numerous French purchasers.

The demand for oil and the pressure upon the market were also seriously increased by the fact that a Royal Decree regulating the payment of debts in the earthquake-districts gave to sellers the right to declare null and void any contracts for sale for future delivery into which they had previously entered. By far the larger number of the sellers of bergamot oil in Calabria have availed themselves to the fullest extent of this permission, and as a result both the foreign and Italian buyers were compelled to appear in the open market for large quantities of oil which they had previously secured by contracts for future delivery. This naturally increased the demand considerably. A new price-level of about 34 marks per kilo was quickly established, and the article has remained at this level, with fluctuations upwards to 35 marks and downwards to 33 marks.

The high prices induced the makers to take up the manufacture again as quickly as possible, and although the total yield will probably remain 25 % below that of an average year, it may safely be estimated that the present stock in Italy amounts to from 7000 to 10000 kilos, as a result of the restricted requirements abroad caused by the high price. If it is taken into consideration that this stock must suffice for nearly 4 months' consumption, and further that experience shows that the supply of bergamot oil is never entirely brought to market, because many owners cannot bring themselves to part with their holdings, it is safe to forecast that at the commencement of the new crop all the available oil will be disposed of.

Unfortunately the prospects of the new harvest are very unfavourable. The past winter has been unusually severe: storms and violent rainfalls have stripped the trees of their foliage and impeded their development, hence the flowering was poor. The later development of the fruit also has taken place under unfavourable conditions. For this reason the news from almost all the producing districts is bad, although it is true that the reports from different centres vary considerably; in some an almost normal yield is reported as probable,

but in most a shortage of from 33 to 50 % is said to be likely, This unusual state of things makes it of course extraordinarily difficult to take a precise survey of the general average; but we shall probably be near the truth in placing the average output at scarcely above two-thirds of a normal crop.

In the case of oil of lemon, only the principal centre of collection, Messina, was destroyed, while the extensive producing area remained almost free from damage by earthquake; on the other hand, in the case of bergamot oil, the entire producing country was ravaged by shocks, and it will therefore be desirable to add a word concerning the present conditions in Southern Calabria: —

The manufacture of oil of bergamot invariably takes place on small farms which are scattered round about the numerous towns, townships and villages of Southern Calabria. All these places have been more or less destroyed by the earthquake, and a large part of the population is buried under the ruins. But as everywhere the communities were small (even in Reggio the number of survivors probably does not exceed 20000), it was much easier here than it was in Messina to procure new dwellings for the remaining people, and to-day the visitor to Calabria sees everywhere in the earthquake-region round about the older townships new and more or less pleasantly built settlements of sheds. In Messina scarcely one-third to one-half of the survivors have returned to the quarter of the town where the sheds have been erected, and these are mostly of the poorer classes; but in Calabria it may be said that the whole surviving population has returned, especially the well-to-do. For this reason life in that district was able to resume its normal course much more quickly than was the case in Messina. The soil is again being cultivated; the lemon, bergamot and orange gardens are being tended, and the simple tools required for the bergamot industry have been partly dug up from the ruins and partly replaced by new ones; in short it may be asserted that, in common with other occupations, the bergamot oil industry has here again overcome its initial difficulties and is now able to go on as before.

Lemon Oil. The panic which seized upon all consuming countries immediately after the Messina earthquake, and the fear of a shortage of oil of lemon, had driven up the prices of this article to figures never previously known, but they quickly fell from this pinnacle when the reports of the Sicilian exporters made it known that the production of oil of lemon had been scarcely affected. Towards the end of March the price had again fallen to a level corresponding to the real conditions, that is to say 7 marks to 7.25 marks per kilo, and it was to be expected that any renewed increase would be prevented by the

abundant output of oil, which was moreover stimulated by the slow sale of lemons in boxes. But the position suddenly changed when news was received from the United States of a projected new duty, this news being accompanied by large orders for shipment. In the course of a few days the price of lemon oil rose to 8 marks and 8.25 marks per kilo, and at this point it remained for nearly 4 weeks. A slackening gradually set in when it was shown that there would be no difficulty in supplying the large quantities of oil demanded by the United States. It became more and more evident that the oil-output was far from having been injuriously affected by the earthquake, and that the quantity produced was indeed exceptionally abundant. Thus the prices slowly receded again, and at the beginning of June they reached the lowest point, viz., 6.75 marks. Here, however, they only remained a short time, and by degrees they again rose to 7 marks and 7.25 marks. Now that it is a little easier to review the stocks and that the conviction has gained ground that there is still an available supply of from 100000 to 120000 kilos of lemon oil, the article has fallen once more, and at the present time the price is from 6.25 marks to 7 marks. Out of the stock mentioned above from 3 to $3^1/_2$ months' consumption will have to be satisfied and although at the arrival of the new crop this is hardly likely to be altogether used up, it may be assumed that a very considerable part of the supplies now in existence will find their way abroad.

The news of the prospects of the new crop is, generally speaking, unfavourable. Taking one thing and another the information from the various districts is to the effect that the yield is likely to fall about 20 % below that of last year. Up to the present the quality of the fruit is said, on the whole, to promise very satisfactory results, which means that it is probable the lemons will be suitable for export in cases, but unfavourable climatic conditions may bring about a considerable change in this respect. So far, few contracts for new season's oil for future delivery have been made; the manufacturers ask 6.50 marks for such oil, and presupposing that business will take a normal course, it may be assumed that this will be about the range of the new season's prices, and that no important fluctuations either upwards or downwards are to be expected.

Mandarin Oil. The supplies of this oil are also almost entirely cleared, only a few isolated parcels of good quality being available. The quotations, which rose to 40 marks immediately after the earthquake, have receded to from 28 marks to 30 marks in the course of time, and at this range they still remain. The new crop promises a normal yield, and important changes in prices are hardly to be expected.

Orange Oil, bitter. The stock of old oil has been almost entirely consumed and the new crop looks very unpromising; prices therefore remain exceedingly high.

Orange Oil, sweet. The market development in this article has brought surprises which could not be foreseen. As it became known at an early period that a very large part of the supplies existing in Messina and Reggio had been destroyed by the earthquake, and as moreover the manufacture of orange oil is usually concluded by the end of the year, there was every ground for anticipating a great scarcity of sweet orange oil and a corresponding increase in the prices. Instead of this expectation being realised, the quotations during the past six months have fallen almost uninterruptedly. Only after prolonged and most careful investigation was it possible to discover the explanation of this remarkable and entirely unexpected occurrence. It then became evident that, although in fact after the earthquake only small stocks of oil were left, a quite considerable industry in manufacturing new oil had gradually sprung up.

Usually there is in the first months of the year a flourishing export of oranges in truckloads from Calabria to Northern Italy and foreign countries, but the repeated destruction of the railway-track in Southern Calabria, the blocking of the line with consignments of all kinds of material required to alleviate the distress in the earthquake-region, and last but not least the circumstance that hundreds and hundreds of railway cars had been seized throughout the afflicted region and turned into dwellings for the homeless population, stopped this trade in oranges almost completely. The proprietors of orange-gardens, unable to turn their fruit into cash in the accustomed manner, were therefore compelled to employ it for the manufacture of essential oil. Although in ordinary times the small oil-content of the fruit during the months when it has attained complete maturity makes the preparation of oil entirely unremunerative, this unsatisfactory mode of disposing of the material was the only possible one in the circumstances. The quantity of oil produced under these conditions was so important that it has not only sufficed to supply completely the demand from abroad, but that at the present time there are still about 15000 kilos left in stock.

A steady fall in the oil-prices was unavoidable in these circumstances. Important purchases by America caused an upward movement at about this time, which sent prices up to about 14,50 marks. This upward movement was supported and prolonged by the unfavourable news with regard to the coming crop, which is likely to fall not inconsiderably below a normal harvest, and even the residual stock of the old crop which will be left two months hence will not

be sufficient to bring the total quantity of available oil for the coming year up to the level of an average crop.

On the other hand it must be remembered that the placing of a considerable import-duty upon orange oil in the United States has introduced into the situation a new factor, the effect of which cannot yet be calculated. There can be no doubt that at the present time the stock of sweet orange oil in the United States is comparatively important, but it is a question to what extent this fact, coupled with the increase in the duty, will restrict the future demand for new oil in the United States. Presumably the market-price of the new crop will be determined by the manner in which this problem is solved. Up to the present time the growers' demands for future delivery are maintained at the level which has ruled so far.

Lemon Oil. Within the past few years the researches into the domain of the chemistry of terpenes have brought to light such an abundance of material for the identification of hitherto unknown, and the breaking-up of known, terpenes and terpene derivatives, that the time has appeared to us to be ripe for a fresh investigation[1]) of the terpene-mixture contained in oil of lemon[2]). After removing the oxygenated constituents of the sample under examination by treatment with dilute alcohol, the residual portion was found to possess the following constants: $d_{15°}$ 0,8524, α_D + 66° 8′, $n_{D\,20°}$ 1,47078. Fractional distillation yielded two principal fractions, one boiling at 160 to 178°, the other at 250 to 278°. The first consisted of terpenes, the second, and by far the smaller in point of quantity, of sesquiterpenes.

By careful fractionation the terpenes were subdivided into 15 parts. As the b. p. increases the rotation and the d-limonene-content of the samples also increase, while the sp. gr. falls. It was possible to separate the d-limonene from all fractions in considerable quantities as tetrabromide (m. p. 104 to 105°). The highest yield was given by the fractions boiling at 175 to 178°, where 10 g. oil produced 8,5 g. tetrabromide.

The fractions with the lowest boiling points contain minute quantities of pinene and camphene. We were again able to confirm the presence of l-camphene. Pinene occurs in the oil both in the

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[1]) Comp. Bericht October **1888**, 17; Report April **1893**, 30; October **1893**, 19; October **1894**, 26; April **1896**, 30; October **1896**, 38; April **1897**, 20; October **1897**, 26; April **1898**, 24; October **1898**, 23; April **1899**, 21; October **1901**, 23; April **1902**, 33; October **1902**, 37; October **1903**, 33; October **1904**, 28; April **1905**, 31; October **1908**, 61.

[2]) The results of this investigation have been published in a more detailed form in the Wallach Jubilee-publication (Göttingen 1909. Vandenhoek & Ruprecht) p. 439, under the title, E. Gildemeister and W. Müller, Zur Kenntnis der Bestandteile des Citronenöls.

active and the inactive form, l-α-pinene forming by far the greater part. The last named substance was traced by oxidation into active pinonic acid. The spec. rot. of the free acid was about — 65° in a 5 % chloroform solution. Pinonic acid semicarbazone, m. p. 204°.

The presence of phellandrene was detected in our laboratory as far back as 1897[1]) by means of the nitrite, m. p. 102°. We were also able to determine the presence of β-phellandrene by oxidation with permanganate. This test yielded a liquid glycol, which was converted, by boiling with dilute sulphuric acid, into a hydrated cuminic aldehyde, the semicarbazone of which had a m. p. of 203 to 204°.

β-Pinene.

Oxidation with permanganate with the addition of caustic soda yielded a sparingly soluble sodium salt, the best yield being obtained from the fraction boiling between 165 and 168°. This salt was found to be sodium l-nopinate. The oil which had remained unaffected by the oxidising process contained, in addition to an intact hydrocarbon, small quantities of nopinone (semicarbazone m. p. 187 to 188°). The nopinate of sodium which was separated out from the oxidation liquors was recrystallised from water, and the nopinic acid contained therein liberated. Recrystallised from benzene, the acid was found to have m. p. 126°, $[\alpha]_D$ — 15,88° in an 11,4 per cent. ethereal solution. The nopinate of sodium was again oxidised into nopinone by permanganate with the addition of sulphuric acid. The ketone was dextrorotatory, its semicarbazone melted at 188° and proved to be identical with the similar body from French oil of turpentine and from oil of hyssop.

It is remarkable that β-pinene could be detected in this manner in all the fractions, even in those with the highest boiling points. The slight rotation of limonene is therefore mainly due to the presence of this lævorotatory hydrocarbon in addition to d-limonene.

γ-Terpinene.

In the course of the process of oxidation with permanganate with the addition of free alkali, all the fractions boiling at 173° and higher yielded, besides nopinic acid, a body which was very sparingly soluble in water. Recrystallised from 25 per cent alcohol, and heated rapidly, it was found to melt at 237°. All the fractions only yielded minute quantities of the substance. The body was identified by the erythritol of γ-terpinene, and this result was confirmed by a comparison with erythritol from other sources.

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[1]) Report October **1897**, 26.

When boiled with dilute sulphuric acid, the erythritol gave off water and was converted into thymol and carvacrol. B. p. 232 to 236°, $d_{15°}$ 0,9841, $\alpha_D \pm 0$, $n_{D20°}$ 1,52320. The nitroso-compound was not suitable for the identification of the phenols, for it was impossible to obtain bodies of a uniform melting point. The urethanes were therefore used for identification purposes, their different solubilitys in petroleum ether making separation possible. The phenylies urethane, m. p. 136°, sparingly soluble in petroleum ether, was found to be identical with carvacrol phenyl urethane. The portion which dissolved readily in petroleum ether was thymol phenylurethane, m. p. 103 to 104°.

Upon oxidising the erythritol with chromic acid we obtained a mixture of oily substances which gave no reaction with semicarbazide. Oxidation with permanganate (6 g. erythritol dissolved in 400 cc. water, 12 g. potassium hydroxide, 21,5 g. of potassium permanganate and 500 g. ice) produced principally two solid, non-volatile acids, of which one, m. p. 97 to 98°, was identical with oxalic acid. Of the second acid, m.p. 147 to 149°, only the very smallest quantity had been obtained. When heated in a test tube it gave off carbon dioxide gas. It may possibly be identical with *iso*-propyl tartronic acid, which has been prepared by Bruner, and of which the melting point is stated to be about 149°.

When shaken with alkaline bromine liquor the erythritol yielded a highly volatile brominated body, crystallising out from alcohol in large flakes, m. p. 93 to 94°. All these reactions, which are illustrated by formulæ in the Wallach Jubilee-publication, agree with the erythritol possessing the constitution of a 1,2,4,5-tetrahydroxy hexahydrocymene. Thus, the identification of γ-terpinene is made quite simple, even small quantities being readily traceable.

Bisabolene.

The sesquiterpene fractions of lemon oil were found to possess the following properties: — b. p. 110 to 130° (7 to 8 mm.), $d_{15°}$ 0,9108, α_D — 28° 14′. One fraction, m. p. 110 to 112° (4 mm.), $d_{15°}$ 0,8813, α_D — 41° 31′, $n_{D20°}$ 1,49015, agreed with the sesquiterpene which had already been isolated by us previously. By passing hydrochloric acid into the ethereal solution a tri-hydrochloride, crystallising in flakes, was obtained. This body melted at 79 to 80° (79,5°), $\alpha_D \pm 0$ in a 5 per cent. chloroform solution. The hydrochloride was converted according to Wallach's method, with sodium acetate and glacial acetic acid, into the hydrocarbon: — b. p. 261 to 262° (751 mm.), $d_{15°}$ 0,8759, $\alpha_D \pm 0$, $n_{D20°}$ 1,4901.

This sesquiterpene is identical with bisabolene, which was discovered by Tucholka[1]) in the oil of Bisabol Myrrh, and also identified by him

[1]) Arch. der Pharm. **235** (1897), 289; Report October **1897**, 36.

from its trihydrochloride, m. p. 79,3°. Tucholka was not quite clear as to the particular class of terpenes to which his hydrocarbon belonged, although its whole behaviour pointed to a sesquiterpene with three double linkings. Hence, Charabot, Dupont and Pillet, in their book *Les huiles essentielles* as well as Schreiner in his monograph on *The Sesquiterpenes*, class it without more ado among the sesquiterpenes. Burgess and Page afterwards discovered in lime oil a sesquiterpene which they called limene, and which also gave a tri-hydrochloride, melting at 79 to 80°. Tucholka's work and the other literature referred to must have been unknown to these two investigators, otherwise they would certainly have compared the sesquiterpene of lime oil with bisabolene, before endowing chemical literature with another new name[1]).

A fraction with a higher boiling point yielded a very minute quantity of a hydrochloride, melting at 105°. After repeated recrystallisation from alcohol its m. p. did not rise beyond 110 to 113°. The behaviour of this body points to cadinene dihydrochloride.

Our investigation therefore shows that, in addition to d-limonene, which has long been known as the principal constituent, the only body which occurs in the oil in relatively considerable proportions is l-β-pinene. Of l- and i-α-pinene, l-camphene, β-phellandrene and γ-terpinene only small quantities were discovered; p-cymene could not be detected at all. The sesquiterpenes only form a very inconsiderable proportion of the oil, which probably, besides bisabolene, also contains cadinene.

Orange Oils. We have lately examined in our laboratory some orange oils produced in Jamaica; all of them had a good, intense odour, and the samples which were pressed from sweet fruit also agreed in their constants (apart from a slightly smaller residue of evaporation) with Italian oils. The two samples of bitter oil on the other hand were somewhat lighter, and showed a higher optical rotation than is usually the case. Perhaps the cause of this lies in their source of production. But as it is possible that the variations referred to may be due to the addition of sweet to bitter oil, it is not out of the question that insufficient care has been taken in selecting the fruit for pressing.

On the basis of numerous experiments with authentic oils we have been able, several years ago, to trace clearly defined differences in the constants of sweet and bitter orange oils of Italian origin.[2]) The following table clearly indicates the points in which Jamaica oils agree with and differ from the Italian varieties:

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[1]) In the article which appears in the Wallach Jubilee-publication, further details and a general compilation are given.

[2]) Report October **1906**, 35.

	Orange oil, sweet		Orange oil, bitter	
	Jamaica	Italy	Jamaica	Italy
$d_{15°}$	0,8481 0,8488	0,848 to 0,853	0,8517 0,8521	0,853 to 0,857
$\alpha_{D20°}$	+ 97° 47′ + 98° 2′	+ 95° to + 98°	+ 96° 20′ + 96° 58′	+ 90° to + 93°
α_D of the first 10%	+ 97° 4′ + 96° 54′	not, or only slightly, lower	+ 96° 40′ + 95° 53′	slightly higher
Residue of evaporation	1,4%; 1,4%	2 to 4%	2,6%; 3,2%	3 to 5%

P. Bohrisch [1]) in a paper on phosphorated oil, discusses among other matters what substances are best suited for preserving this oil, and among these he mentions limonene, which was first recommended for this purpose by Schweissinger.[2]) Bohrisch has discovered that only limonene manufactured from sweet oil of orange has a conserving action upon phosphorated oil, and that limonene from caraway oil is of no effect. From these experimental results it appears to us to be evident that limonene possesses no deoxidizing power whatsoever, as otherwise it would be inexplicable why limonene from oranges should behave altogether differently from limonene from caraway, with which it is identical. Our opinion is that the conserving power of limonene from oranges, as shown in the results obtained by Bohrisch, is due to bodies which were present in the commercial article as impurities.

The statement of Bohrisch that limonene is almost insoluble in paraffin oil is incorrect; on the contrary, limonene is soluble in this oil in every proportion, and if any turbidity occurs it is due to the small proportion of water in the limonene and disappears again very quickly when the solution is shaken up with anhydrous sulphate of sodium.

For the determination of the citral-content in oil of lemon, see Analytical Notes.

Eucalyptus Oils. Business in all commercial varieties was exceedingly quiet and the transactions have not exceeded the ordinary limits of consumption. Supplies of *Globulus* oil were abundantly offered, and the ordinary qualities containing phellandrene, which are included in our lists under the general description of "Australian Eucalyptus oil" occasionally accumulated heavily. This variety, however, owing to its powerful aromatic odour, is rather suitable for the manufacture

[1]) Pharm. Zentralh. **50** (1909), 618.
[2]) Ibidem **43** (1902), 259.

of cheap soaps. Generally speaking the sale of eucalyptus oil is rather suffering from the competition of eucalyptol, which is now so cheap, and the advantages of which have been expounded by us at length on various occasions.

From the Transvaal we have received a sample of Eucalyptus oil which, judging by the odour and by its content of cineol, might have been a crude *Globulus* oil. Its constants also lie within the limits laid down for oils of this class: $d_{15°}$ 0,9236, α_D + 1°45′, $n_{D20°}$ 1,46337; it was free from phellandrene, soluble in 2,8 vols. of 70 per cent. and more alcohol, and had a cineol-content of about 65%.

H. D. Baker[1]) reports on the use of eucalyptus leaves in Tasmania and calls attention to a new use for eucalyptus trees. Eucalyptus oil is distilled in Australia for medicinal purposes, and in New South Wales acetic acid is gained as a bye-product in this industry, but at Port Esperance the oil is obtained as a bye-product in the preparation of a more valuable extract. This extract is used as a preservative for boilers. It is miscible with water and frees the boiler from any acid and from fatty bodies and salts by forming an innocuous precipitate with these destructive ingredients and preventing incrustation. Four tons of eucalyptus leaves give one ton of extract and 70 to 80 lbs. of eucalyptus oil.

Erucalyptus leaves are also recommended for use in gas manufactue. It is said that the bark can be employed in paper and tannin manufacture, as well as for leather-dressing, and the wood is very suitable for railway sleepers.

Geranium Oil. In the course of the summer only few, if any, changes have taken place in the geranium oil market. The prices of Algerian oil remained completely unaltered and in spite of all rumours that the greater part of the cultivations have been abandoned, offers were not lacking. A few important producers showed themselves very ready to make concessions, although they maintained that they were only in a position to sell cheaply because they had been able to obtain considerably higher prices for the greater part of their output by having sold it previously when the market was better. This probably refers to contracts running over several years, which have probably not turned out very satisfactorily for the buyers. The exports during the first 7 months of the last two years were as follows: —

1909 26700 kilos, value fr. 58900,
1908 24600 „ „ „ 54100.

The average value in 1909 was 22 fr. per kilo!

[1]) Daily Consular and Trade Reports, No. 3415, 25. Febr. 1909, p. 13.

Neither has the position of Réunion geranium oil undergone any improvement in the meantime. Offers at 19 fr. were not rare, but even they only received casual attention. The Syndicate continues to pile up supplies in Europe, but in spite of all its efforts it is still waiting in vain for the golden days.

The output continues to be increased in a senseless manner, for whereas in the first half-year of 1908 19316 kilos were shipped, the exports in the corresponding period of the current year amounted to not less than 32870 kilos, or almost double last year's quantity. Where these quantities are to find a market remains a problem.

East Indian geranium oil will henceforth be dealt with by us under the headings Palmarosa Oil or Ginger grass Oil, because these products, which are distilled from grasses, cannot properly be classed as geranium oils.

Ginger Grass Oil. Very little of good quality has been shipped, hence the supplies in Europe have remained short and the prices firm. For the moment offers are again entirely wanting and just at present it is impossible to form a judgment of the future of the article.

Ginger Oil. In the course of the last few months the supplies of raw material suitable for oil preparation have been very scanty, and there has been a serious want of the cheaper varieties in general. Only the most urgent requirements in ginger oil could be covered, and the scarcity has found expression in a not inconsiderable increase in prices. We were only recently able to make a contract for a few important parcels of raw material, but their arrival is not expected for a few weeks to come.

Oil of Hyptis suaveolens Poit. This plant, which belongs to the *Labiatae* and is known on the Philippines in the Tagal language by the name of *sub-cabayog,* yields, according to Bacon[1]) a very small proportion of a green-coloured oil with a strong odour of menthol, which in fact, as was shown by further examination, constitutes the chief constituent of the oil. The slight oil-content (200 kilos material produced only 27 g. or 0,0135 %) excludes the possibility of distillation on a large scale.

As previously reported by us[2]) the yield which was obtained in Java from the same herb is considerably higher, viz., about 1 %.

Hyssop Oil. In another place[3]) we have published in detail the results of our examination of the constituents of hyssop oil, to

[1]) Philippine Journ. of sc. **4** (1909), A, 130.

[2]) Report November **1908**, 74.

[3]) Wallach Jubilee Publication (Göttingen 1909, Vandenhoek & Ruprecht) p. 414: E. Gildemeister and H. Köhler: Über das Vorkommen von β-Pinen und l-Pinocamphon im Ysopöl und einige Beobachtungen über Isomerien in der Pinenreihe.

which occasional allusions have been made in previous reports[1]). It will therefore only be necessary to mention here, for the purpose of completing the record, the results which have been obtained since we last dealt with the matter in our Reports.

As already discovered by us, hyssop oil contains, in addition to β-pinene, an active ketone, l-pinocamphone, which had hitherto not been observed in essential oils. Its oxidation with permanganate resulted in active l-pinonic acid. Notwithstanding that after our experiments in its decomposition we had no doubt as to the character of this ketonic acid from pinocamphone, yet we were unable to give absolute proof of the correctness of our view, because Tiemann had obtained, by dry distillation of α-dihydroxydihydro campholenic acid, an acid $C_{10}H_{16}O_3$, which he regarded as l-pinonic acid, and which possessed quite different properties. We therefore set ourselves the task of preparing the optical antipode of the acid which we had obtained, in order that by combining the two active varieties we might arrive at the well-known racemic pinonic acid.

Among the available data concerning the oxidation of pinene, particulars as to the rotation of the turpentine oil fractions employed are unfortunately almost wanting. The principal product obtained from them was always racemic pinonic acid. We proceeded from the assumption (which was confirmed by the experiment) that it must be possible, by using pinene of high rotatory power, to obtain the active acid as the principal constituent. For this purpose we employed d-pinene from Greek oil of turpentine, with the following properties: — b. p. 156° (760 mm.), $d_{15°}$ 0,8642, α_D + 40,23°, $n_{D20°}$ 1,46565. The specific rotation $[\alpha]_D$ + 46,73° which was calculated from the above is the highest value which has thus far been observed for d-pinene. By oxidising with permanganate the active d-pinonic acid was obtained in the form of a viscous yellow oil, b. p. 168° (12 mm.), α_D + 27°. The acid soon solidified. M. p. 68 to 69°, $[\alpha]_D$ + 88,27° in a 5,647 per cent. chloroform solution. The properties of the derivatives conformed completely to those of the lævorotatory acid. The semicarbazone melted at 204°, the oxime at 129° and the d-metho-ethyl heptanonolide, which was formed by rearrangement with sulphuric acid, at 47 to 48°. Mixing of equal quantities of the two optically isomeric acids led to the well-known racemic pinonic acid (α-pinonic acid) of which the m. p. was found to be 103 to 104°. By uniting the two active oximes melting at 129° there was formed the racemic oxime, m. p. 150°, while mixture of the two ketolactones produced racemic metho-ethyl heptanonolide, m. p. 63 to 63,5°, a substance which has long been known. These experiments conclusively show

[1]) Report April **1908**, 59; April **1909**, 120.

the acid contained in oil of hyssop to be l-pinonic acid, and the ketone l-pinocamphone.

We cannot omit here to lay stress upon the fact that the former practice of neglecting to observe the rotation of the primary material has helped to delay very considerably the solution of certain problems existing in connection with the pinene series. It will be advisable, in the case of future examinations, either to start with entirely inactive pinene, or to use as primary material substances of the highest degree of optical purity obtainable. For instance, it is stated in the literature on the subject that active oil of turpentine yields racemic pinol hydrate, but when we used highly active pinene, active pinol hydrate, m. p. 150°, was very easily formed.

In a discussion on the investigations of essential oils published during the year 1908, Jeancard and Satie[1]) refer among other matters, to our statements as to the constants of hyssop oils distilled by us[2]). For purposes of comparison they set out the properties of two oils which they had obtained at Cannes in 1903 and 1908 from green, flowering herb. These oils deviated very greatly from our distillates as regards rotation and solubility. Their behaviour was as follows: —

Distillate 1903: $d_{15°}$ 0,9252, α_D + 1° acid no. 0,8, ester no. 9,2, ester no. after acetylation 70,0.

Distillate 1908: $d_{15°}$ 0,9262, α_D — 2°6′, acid no. 0,8, ester no. 11,9, ester no. after acetylation 51,1.

The constants observed by us in our own distillates were as follow: —

$d_{15°}$ 0,925 to 0,940, α_D — 17° to — 24° 18′, acid no. up to 3,1, ester no. 1,4 to 11, ester no. after acetylation 37 to 45.

Our distillates required from 1 to 8 vols. of 80 per cent. alcohol to give a solution, and this solution was not even then always quite clear, owing to the separation of paraffin, but the oils obtained by Jeancard and Satie were soluble in 70 per cent. (2 to 2,5 vols) and 65 per cent. (8,5 to 9 vols) alcohol respectively. The last-named point of difference may possibly be due to the manner of distilling, but as regards the great difference in rotation we are at present at a loss for an explanation. Jeancard and Satie ascribe it to the fact that they used fresh, whereas we used withered for material distilling. This explanation is contradicted by the observation made by us that there is not the slightest difference in constants between oil from quite fresh and from faded herb. We therefore think that an explanation of the differences must rather be sought in botanical differences between the plants distilled.

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[1]) Americ. Perfumer **4** (1909), 84.
[2]) Report April **1908**, 58.

We may also point out that the constants of most of the commercial oils from the South of France which have been examined by us agree with those of our own distillates, although as a rule in the case of the French oils the rotation is slightly lower, occasionally falling to — 11°. In the case of oils where the rotation was still lower we were able to observe a pronounced odour of spike oil, which increased in proportion as the rotation diminished. In one particularly striking instance we were able to prove adulteration with spike oil. This adulteration was indirectly admitted by the distiller, who explained that spike had been previously distilled in the same still, and that this might possibly have produced contamination. Such experiences are sufficient reason for us to regard with distrust hyssop oils of which the rotation is exceptionally low.

Jasmine flower Oil. When jasmine flowers are extracted with petroleum-ether the result, as is well known, is the so-called concrete oil of jasmine flowers (*essence naturelle concrète de jasmin*). This consists only partly of volatile oil [1]): the bulk is a mixture of wax-like bodies. L. G. Radcliffe and J. Allen [2]) have examined this wax and found it to possess the following constants: sol. point 56 to 57°, sap. no. 65,8 (the wax being very difficult to saponify, it was necessary to carry out the work in a solution of amylic alcohol), iodine number, according to Wijs, 52 to 53. The high m. p. of the wax made the examination in the Zeiss butter refractometer more difficult, but determinations were taken at various temperatures between 56 and 84°. As an example, the authors discovered that at 62° the scale registered 40 (Lewkowitsch gives 29,5 to 30 at 30° for beeswax). No separate constituents were determined.

Juniper Oil. The crop reports from Italy and France are uniformly unsatisfactory, but in Hungary the yield is a normal one. Naturally, the Hungarians are trying to make the best possible use from this absence of competition, and demand exceedingly high prices. Since the beginning of the season the prices have already advanced several marks, but whether the value can be permanently kept up or not depends upon the demand. It will not be advisable to count upon lower prices for juniper-berry oil of our distilling.

The principal constituents of Juniper berry oil are the hydrocarbons pinene [3]) and cadinene [4]). An examination which has been conducted by us into the oxygenous compounds of the oil has shown them

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[1]) Report October **1904**, 49.
[2]) Journ. Soc. chem. Industry **28** (1909), 227.
[3]) Wallach, Liebig's Annalen **227** (1885), 288.
[4]) Report April **1890**, 58.

to consist in great part of the alcohol terpinenol, which also occurs in oils of cardamom and majoran. The sample of juniper oil which was used by us for the purposes of investigation had the following constants, viz., $d_{15°}$ 0,8740, α_D — 7° 20′, sap. no. 7,2. In order to recover the oxygenated portions of the oil, which are more readily soluble in dilute alcohol than are the hydrocarbons, the sample was extracted repeatedly with 70 per cent. alcohol, and the body which was found in the alcoholic extract recovered after the solvent had been distilled off. It appeared in the form of an oil possessing a pleasant odour of juniper berries, and was found to possess the following constants: $d_{15°}$ 0,9300, α_D — 3° 44′, sap. no. 21,8, sap. no. after acetylation 136, corresponding to 41,65 per cent. alcohol $C_{10}H_{18}O$. The alcohol-content, determined by Boulez' method[1]), was 56,2 % $C_{10}H_{18}O$. When the oil was fractionated (8 mm.) 70 % passed over between 86 and 110°, while 30 % distilled between 110 and 155°. From the principal part a portion was separated by repeated fractionation. This was found to consist in the main of terpinenol-4, and possessed the following constants: b. p. 93 to 95 (8 mm.) 215 to 220° (750 mm.); $d_{15°}$ 0,9400; α_D + 13° 6′. Oxidation of this fraction with diluted permanganate of potassium, under cooling, gave a glycerin, 1, 2, 4-trihydroxyterpane, m. p. 114 to 116°, which had already been obtained by Wallach[2]) from terpinenol-4.

Analysis: 0,1350 g material: 0,3150 g CO_2, 0,1256 g H_2O:

	found:	calculated for $C_{10}H_{20}O_3$:
C	63,64	63,83 %
H	10,34	10,63 %

When this glycerin was boiled with dilute sulphuric acid there was formed, in addition to cymene, carvenone, which was identified from its semicarbazone, m. p. 202°. When further oxidised with permanganate, the glycerine also yielded α, α'-dihydroxy-α, α'-methyl *iso*-propyl-adipic acid, m. p. 205°. Inactive acid was probably mixed with this body, because when it was boiled with hydrochloric acid the result was not the dilactone of the active acid, melting at 63 to 64°, but the dilactone with m. p. 73 to 74°, which, according to Wallach, is a derivative of i-α, α'-dihydroxy-α, α'-methyl *iso*-propyladipic acid. Part of the principal fraction was warmed up with twice its quantity of 100 % formic acid, when water was given off, and hydrocarbons produced, which partly distilled at 180°. When the hydrocarbons were oxidised with diluted solution of permanganate the resultant products were the erythritol, m. p. 237 to 238°, characteristic of γ-terpenene and i-α, α'-dihydroxy-α, α'-methyl *iso*-propyladipic acid, m. p. 188°,

[1]) Comp. Report April **1907**, 120.
[2]) Liebig's Annalen **362** (1908), 278; Report November **1908**, 179.

which occurs in the process of oxidising α-terpinene. Attempts to obtain crystallising derivatives from the terpinenol, or to separate it from the accompanying bodies in a still purer form, have so far led to no result. Another alcohol occurs in juniper oil in addition to terpineol, but in far smaller proportions than that body. This alcohol possesses the following constants: b. p. 105 to 110° (8 mm.) 218 to 226° at atmospheric pressure, $d_{15°}$ 0,9476, α_D —4°30′, $n_{D22°}$ 1,48248. It combines readily with phthalic acid anhydride, and was isolated from the fractions boiling between 95 and 130° in the form of the acid phthalic ester. In its odour the alcohol reminds of geraniol and borneol, and it is probably a mixture of various alcohols. Besides the compounds enumerated above, juniper oil contains bodies of a particularly characteristic odour, most of which occur in small proportions in the fraction boiling between 72 and 88° (8 mm.).

Oil of Lantana camara L.[1]. According to Bacon[2]), the parent plant of this oil, which belongs to the *Verbenaceæ* and possesses a pleasant odour, flourishes with such extraordinary profusion in the Philippines that it would undoubtedly pay to cultivate it. The yield of oil from the leaves appears to vary greatly according to age, season, etc, as from two parcels of raw material, one weighing 60 and the other 110 kilos, the oil-yield was 0,07 and 0,245 per cent. by volume respectively. The oil is pale yellow, with an odour reminding of sage, and has the following constants: $d\frac{30°}{4°}$ 0,9132, $\alpha_{D30°}$ +11,5°, $n_{D30°}$ 1,4913. Subjected to fractionation, 50 g. oil resulted as follows: — 22 g., b. p. 125 to 130° (12 mm.), $n_{D30°}$ 1,4892; and 24 g., b. p. 130 to 140° (11 mm.), $n_{D30°}$ 1,4970.

Last year[3]) we described a West Indian oil of *Lantana odorata* L. With the exception of the rotation, its properties agree closely with those ascertained by Bacon for oil of *Lantana camara* L.

Lavender Oil. All reports from the departments of the Basses-Alpes, Alpes-Maritimes, Vaucluse, and Drôme — which are the chief lavender districts —, agree in stating that in the early spring the highest expectations of the success of this year's crop were being entertained. During the greater part of the winter months a thick cover of snow protected the vegetation from the effect of a too high degree of cold, and it was therefore fair to expect a healthy development of the plants in the spring. Unfortunately severe frosts in May have had an exceedingly injurious effect. The first young shoots were destroyed and, owing to the continuation of unfavourable weather, were unable to renew themselves. The drought which has prevailed

[1]) Compare Gildemeister and Hoffmann, *The Volatile Oils* p. 594.
[2]) Philippine Journ. of sc. **4** (1909), A, 127.
[3]) Report November **1908**, 140.

during the flowering time has finally destroyed all expectations of a normal crop, and we now have to make the best of a most unfavourable result. The yield is estimated at about one-third of that of last year. Contrary to their previous habit of rushing up the prices, the distillers were only willing to pay from 7 to 10 fr. for the flowers, because business in the article was exceedingly lifeless, and because the presumption is that in the near future the demand for lavender oil will not be large enough specially to tax the resources of the suppliers. In the expectation of an increase in the duty of lavender oil in the new American Customs Tariff, and taking advantage of the low prices in the early part of the year, such quantities are said to have been shipped to the United States that the requirements of this important consuming market are richly provided for the next 2 years. If this rumour should turn out to be well-founded, there is the possibility that the failure of the crop will in the long run only have a slight effect upon the course of prices. At the first market held at Digne on 4th September, however, very high rates were asked, but only a few transactions were concluded, as the buyers, who were numerously represented, refused to concede the demands. Reliable information as to the course of prices will not be available until after the next following markets at Apt and Sault.

During the gathering of the crop our works at Barrême were fully occupied. Although there was some difficulty in obtaining a sufficiency of material, we have again been able to distil a considerable quantity of oil, to the exquisite quality of which we again call attention; the ester-content, however, is this year a little less than formerly. It remains to be added that our stocks are not important, and that they may soon be off our hands.

We have distilled a few grammes of oil of lavender from a small quantity of Barrême lavender plants which have flourished comparatively well in the Alpine garden of our works at Miltitz. This oil agreed with the oil obtained by us in Barrême, and, like it, was distinguished by a high ester-content. It had a good and intense odour, a pale yellow colour, and only the solubility left a little to be desired, which is possibly due to the difference in soil. The constants of the oil were as follows: — $d_{15°}$ 0,8888, α_D — 8° 40′, $n_{D\,20°}$ 1,46010, acid no. 0,5, ester no. 157,6, corresponding to 55,1 % linalylacetate. It gave a cloudy solution in 10 vols. or more of 70 % alcohol.

Lemongrass Oil. Since our last Report prices of this oil have only shown unimportant fluctuations, and they remain to-day practically unchanged at about 2 d. for future delivery and 2 1/4 d. for prompt delivery. The shipments from Cochin between 1st July 1908 and 30th June 1909 have been as follows: —

To London	663½	cases
„ Liverpool	860	„
„ Havre	213	„
„ Marseilles	1637½	„
„ Hamburg	215	„
„ New York	1166	„
Total	4755	cases
against	6082	„ in the corresponding period of 1907/8,
„	6239	„ „ „ „ „ „ 1906/7,
„	2259	„ „ „ „ „ „ 1905/6.

Although, therefore, the shipments during the last season have fallen much behind those of the two previous years, it was not possible to drive up the prices, a fact which sufficiently proves that the output is more than enough for the normal requirements of the world. This applies with the more force because supplies are also to be expected from other quarters, and these will contribute to affect adversely the value of the article, unless, indeed, new sources of consumption should be discovered.

Of the heavy imports which were consigned to London not many years ago from the West Indian Islands, a few small parcels are still floating about. In dealing with some of these several months ago it was observed that whereas at the time of importation analysis showed them to contain 80% and more of citral, the same parcels contain to-day about 10% less of citral than when they were first analysed, a circumstance which is said to have led to various claims, as the parcels concerned had been resold under the old guarantee.

A lemongrass oil which has been sent to us from the Comoro Islands resembled in its general behaviour the so-called West Indian oils, such as are produced not only in the West Indies but also in Brazil, Africa, Java etc. In spite of its high citral content, which by the bisulphite method was found to be 83%, it only gave a clear solution at first even in 90% alcohol, and when more alcohol was added pronounced turbidity ensued. The optical rotation was 0, the sp. gr. at 15° was 0,8914.

Two samples sent to us by Mr. J. H. Burkill, of Calcutta, and distilled by himself, belonged to the same group of lemongrass oils; their properties are enumerated below: —

According to a written communication by Mr. Burkill the grass which formed the raw material came from the district of Jalpaiguri in Northern Bengal, sample I having been distilled locally and sample II in Calcutta.

I. $d_{15°}$ 0,8954; α_D — 0° 28′; aldehyde content 96% (bisulphite method) or 84% (sulphite method)[1]).

[1]) With regard to the difference in aldehyde-content by the two methods see Report November **1908**, 83.

II. $d_{15°}$ 0,8924; α_D — 0°49′; aldehyde content 87 % (bisulphite method) or 82 % (sulphite method).

Neither oil was soluble in 70 per cent. alcohol, but both dissolved in 0,9 vol. 80 per cent alcohol, although turbidity ensued when more alcohol was added. Their behaviour with 90 per cent., and even with absolute alcohol was similar, the solutions, clear at first, becoming strongly opalescent when diluted.

It is worthy of note that these two oils are of East Indian origin. The term "East Indian" oils, however, is usually applied to the easily soluble distillates which are prepared on the Malabar coast. According to Stapf[1]), the difference exists in the parent plants, the easily-soluble Malabar oils being the product of *Cymbopogon flexuosus* Stapf. and the so-called "West Indian" oils, which are sparingly soluble, of *C. citratus* Stapf.

According to Bacon[2]), a variety of grass which, from the characteristics of the lemongrass oil it produces, is regarded as *Andropogon citratus* D. C., is cultivated to a small extent in the Philippines, although it occurs everywhere throughout the Archipelago, both as a garden-plant and in the wild state, and grows in special profusion in the highlands of the province of Benguet. In the Tagal language this oil-grass is called by the name given to it in 1635 by the Spanish Jesuit Juan Eusebius Nürnberg, who was the first to describe it, viz: *tanglat* or, more accurately, *tañglad.* Other native names for the plant are *salai* and *balyoco*; its Spanish name is *Paja de Meca.* At the present time the oil is not distilled commercially. Bacon points out, quite justly, that under the present market-conditions the cultivation of lemongrass would not be profitable, notwithstanding the fact that it grows quickly and produces a rich yield, and he only recommends it as a temporary crop, to be grown until other plantations produce sufficient returns. A grass 5 months old, distilled two days after being cut, produced 0,2 % of an oil with the following properties: $d\,\frac{30°}{4°}$ 0,894, $\alpha_{D30°}$ + 8,1°, $n_{D30°}$ 1,4857, citral-content 79 %. The oil held Schimmel's test, that is, it dissolved readily in 1 to 2 vols. and in 10 vols. of 80 per cent. alcohol, (there seems to have been some confusion with citronella oil). The same plants, when cut again 4 months later, produced 0,2 % oil with the following constants: $d\,\frac{30°}{4°}$ 0,8841, $\alpha_{D30°}$ + 2,1°, $n_{D30°}$ 1,4765, citral content 77 %, holding Schimmel's test. A grass seven months old from another plantation, distilled immediately after being cut, produced 0,21 % oil, possessing the following constants: $d\,\frac{30°}{4°}$ 0,891, $\alpha_{D30°}$ + 7,76°, $n_{D30°}$ 1,4812,

[1]) Comp. Report April **1907**, 30.

[2]) Philippine Journ. of sc. **4** (1909), A, 111.

citral content 78 %, holding Schimmel's test. Fractionation of this oil resulted in 80 % (in round figures), distilling over in a colourless state between 118 and 133° (16 mm.); the separate fractions which passed over between these limits gave clear solutions with 65 per cent. alcohol, — in what proportion is not stated. On the basis of the quantity of grass produced under experimental cultivation, and also of the oil-yield, Bacon estimates and output of from 230 to 300 kilos of oil per hectare, assuming that three crops can be cut annually. As the cultivation is rather exhausting to the soil, the crop must be changed after 3 years.

Limette Oil. The literature of essential oils contains only sporadic data concerning the properties of West Indian limette oil obtained by hand-pressing (hand-pressed oil of limette; hand-pressed lime oil; ecuelled essence of limes), and it is therefore probable that in many quarters uncertainty prevails as to the properties which the oil should possess. We believe therefore that we shall render a general service by mentioning the properties observed by us in the case of a warranted pure quality of this oil, but in doing so we wish it of course to be understood that pure oils may occur which will vary somewhat in one or another of their constants: $d_{15°}$ 0,878 to 0,901, mostly between 0,880 and 0,884, α_D +32° 50′ to +37° 30′, α_D of the first 10 % of the distillate rather higher, or at most 4° lower, than α_D of the original oil, $n_{D\,20°}$ 1,482 to 1,486, acid no. up to 3,0, ester no. 18 to 30; residue of evaporation 10 to 14 %, in one instance 17,8 %[1]). The oil gave a cloudy solution in 4 to 10 vols. of 90 per cent. alcohol, with separation of wax- or paraffin-like constituents.

Oil obtained by distillation (distilled oil of limette; distilled oil of limes; distilled lime oil) as well as the Italian variety of oil obtained by pressure hardly count as commercial articles. What is known of their properties is recorded in Gildemeister's and Hoffmann's work *The Volatile Oils*, p. 477. In the Report referred to in the footnote we also made mention of a distilled limette oil.

Linaloe Oil. Since April last the prices of Mexican oil have fallen about 2 marks per kilo, but they stubbornly remain at that level. The importers in Hamburg continue to be very firm, and in Mexico — where the linaloe districts have again been visited by a member of our staff — the suggestion of any impending fall in prices is repudiated. Off-and-on small parcels have been sold at Marseilles below the price of the day, but these were mostly of inferior quality and in one case heavily adulterated with terpineol. The excellent linaloe oil from Cayenne (*essence de bois de rose femelle*) also known as azélia oil, was available

[1]) Report October **1904**, 54. This oil also showed the abnormally high acid no. of 6,0.

in sufficient quantities, but the prices remained at their present level. Recently, it is true, large parcels of linaloe wood from Cayenne have been offered in Europe on various occasions, but the unjustifiably high prices have prevented their sale.

Matico Oil. The matico oils which have been distilled lately differ considerably as regards their properties from those produced some years ago. The reason of this is that the raw material previously employed, viz., the leaves of *Piper angustifolium* Ruiz. et Pavon is hardly to be found in commerce nowadays, and that its place has been taken by the leaves of other species of *Piper*, as already stated in our last Report[1]).

This fact lends additional interest to a paper by H. Thoms[2]), read before the 7th International Congress for Applied Chemistry in London on the subject of the examination of matico leaves and matico oil. Thoms has endeavoured to distil matico oil from raw material of which the botanical origin had been determined as accurately as possible. In this attempt he derived valuable assistance from Prof. Gilg, of Berlin, and Prof. Casimir de Candolle, of Geneva. For instance, a parcel of leaves received from the province of Huanuco (Peru) was found upon examination by C. de Candolle to contain the leaves of three different species of *Piper*. The leaves of each species were distilled separately, with the following result: —

1. *Piper camphoriferum* C. D. C. This hitherto unknown species of *Piper* was on this occasion described by C. de Candolle. The oil, which was obtained to the extent of 1,11 %, possessed the following properties: $d_{20°}$ 9,500; α_D + 19° 21′, One third of the oil could be distilled over *in vacuo* at 25 mm. up to 115°. In these fractions camphor and borneol could be detected and were identified respectively by the oxime and the urethane. There were also present in the oil terpenes and a sesquiterpene.

2. *Piper lineatum* Ruiz. et Pavon. This yielded 0,44 % essential oil, the principal portion of which boiled between 140 and 160° (15 mm.) and possessed the following constants: d 0,958, α_D + 8° 45′. Neither camphor nor phenol-ethers could be detected.

3. *Piper angustifolium* var. *Ossanum* C. D. C. The oil (yield 0,87 %) only contained traces of phenol-ethers. When distilled *in vacuo* a camphor mixture separated out which melted at 195° and presumably consisted of camphor and borneol.

From a new species of matico leaves received by Thoms, which consisted chiefly of the leaves of *Piper acutifolium* Ruiz et Pavon, var. *subverbascifolium*, mixed with isolated leaves of *Piper molliconum* Kunth

[1]) Report April **1909**, 70.
[2]) Apotheker Ztg. **24** (1909), 411.

and *Piper asperifolium* Ruiz. et Pavon (this parcel had been described by an American source as derived from *Piper Mandoni*) a yield of 0,8 % of oil was obtained. This oil possessed the following constants: $d_{20°}$ 1,10, α_D + 0° 24′, $[\alpha]_D$ + 0° 21,8′, methoxyl-content 21,8 to 22,1 %, content of acids + phenols 1,5 %.

Freed from acids and phenols, the oil, on being distilled *in vacuo*, gave the following fractions: —

				methoxyl-content
I.	B. p. 70 to 148°	15 mm.	5 g.	0 %
II.	„ 148 „ 153°	15 mm.	11 g.	15,6 %
III.	„ 153 „ 155°	15 mm.	35 g.	22,5 %
IV.	„ 155 „ 158°	15 mm.	43 g.	26,3 %
Residue			2 g.	

In the first fraction, pinene was identified by the nitroso-chloride. The second fraction boiled after repeated distillation over sodium at 147 to 149° (12 mm.) and consisted principally of sesquiterpene. In fraction III, after distillation over sodium, dill *iso*-apiol (m. p. 44 to 45°) was found present. The fourth fraction contained dill apiol, identified as tri-bromo dill-apiol (m. p. 110°). We also distilled similar leaves and placed the oil, as well as a sample of the leaves themselves, at the disposal of Prof. Thoms[1]). The leaves were identical with those referred to above, except in this respect, that in our sample the base of the leave was rounded on both sides, and that the leaves were heart-shaped. Prof. C. de Candolle is of opinion that these leaves represent the lower leaves of specimens of *Piper acutifolium* Ruiz. et Pavon, var. *subverbascifolium*, before flowering.

The following constants were determined: $d_{20°}$ 0,939, α_D + 0° 24′, $[\alpha]_D$ + 0° 25,5′. The oil contained 1 % of acids and phenols and a very large proportion of sesquiterpenes. Its methoxyl-content was 4,2 %.

The oil (200 g.) was split up into the following fractions: —

I.	B. p. 50 to 150°	80 mm.	50 g.
II.	„ 130 „ 155°	22 mm.	100 g.
III.	„ 155 „ 165°	22 mm.	30 g.
IV.	„ 165 „ 175°	22 mm.	7 g.
Residue			4 g.

Pinene was found to occur in fraction I and was identified by the nitroso-chloride. Dill apiol, of which only traces were present, was identified from the bromine derivative.

For the botanical description of each separate species of leaves we refer to the paper, as quoted above.

Oil of Mentha arvensis var. glabrata. F. Rabak[2]) has distilled an essential oil from *Mentha arvensis var. glabrata* Gray. (N. O.

[1]) Report April **1909**, 70.
[2]) The Midland Drugg. and Pharm. Review **43** (1909), 5.

Labiatæ) which grows in South-Dakota. The oil-yield, calculated for green herb, was 0,8 %. The oil was pale yellow, of an odour resembling that of peppermint, but also pointing to the presence of pulegone; the taste was strongly peppermint-like and acrid. The oil dissolved without turbidity in half its vol. of 90 per cent. alcohol, and possessed the following constants: d 0,9267, α_D + 16° 27′, acid no. 2,6 ester 13,1, corresponding to a content of 4,6 % of ester $C_{10}H_{19}OCOCH_3$, ester no. after acetylisation 47, corresponding to 13,57 % of alcohol $C_{10}H_{19}OH$. No aldehydes could be detected either with fuchsine or with Nessler's solution.

Oil of Monarda didyma L. Some time ago[1]) we reported on 2 oils of *Monarda didyma* L. (N. O. Labiatæ) distilled by ourselves, the one from flowers, the other from herb. Last summer we were again in a position to prepare an oil of this kind from half-faded flowers, and found it to possess constants similar to those observed in that distilled a year earlier: $d_{15°}$ 0,8740, α_D — 15°45′, $n_{D20°}$ 1,46743, acid no. 4,6, ester no. 5,6, soluble in 3 vols. and over of 70 per cent. alcohol; after the addittion of 6 vols. of alcohol paraffin began to separate out in abundance. The colour of the oil was lemon-yellow, the odour peculiar, resembling ambergris, and rather faint. The yield of oil equalled 0,26 %.

Oil of Morinda citrifolia. In the fruit of *Morinda citrifolia* L., N. O. Rubiaceae, a native of the tropics, C. J. E. Lohmann[2]) some years ago discovered the presence of one of the higher alipathic acids in conjunction with an ester. This fruit (known locally as *Bengkudu* or *Tjangkudu*), yields an essential oil which was prepared some time ago in Java by A. W. K. de Jong, and which has recently been examined by P. van Romburgh[3]).

The oil was of a yellowish colour, and had a sp. gr. of 0,927 at 13°. It was cloudy, owing to the separation from it of small crystals, which, recrystallised from alcohol, melted at 60°, and, upon analysis, were shown to consist of paraffins. When freed from the crystals the oil was almost entirely soluble in dilute soda-liquor. In the solution *capronic* (m. p. — 5,2°; $d_{15°}$ 0,932) and *caprylic acid* (m. p. 15,2°; $d_{14°}$ 0,913) as well a traces of the higher aliphatic acids, could be detected.

In the neutral part of the oil, which only amounted to a few per cent, ethyl alcohol (identified by the b. p. and the iodoform-test); also probably methyl alcohol and alcohols of a fusel-like odour, could be detected after saponification.

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[1]) Report November **1908**, 86.

[2]) Report Gov. Botanical Gardens, Buitenzorg **1896**, 59.

[3]) Koninklijke Akademie van Wetenschappen te Amsterdam, **1909**, 17. From a copy kindly sent to us.

The percentage of acids is over 90, a rare occurrence with essential oils.

Neroli Oil. As was to be expected from the extraordinarily cold spring weather, the beginning of the distilling season was delayed until the middle of May and the fear expressed in our last Report, that no particularly prolific crop was to be expected, has unfortunately proved to be well-founded. In any case, however, the result was better than 1908, and there should have been no reason for asking higher prices for the flowers than were paid the year before. But the Société coopérative des Producteurs, etc. at first fixed the price of the flowers for the distillers at 1.50 fr. and only reduced this price to 1.40 fr. if 15,000 kilos and 1.35 fr. if 50.000 kilos were taken. As might be expected, the distillers are indignant at this proceeding, and they intend next year to take steps to liberate themselves from the arbitrary influence of the Société. It remains to be seen which party will emerge victoriously from this quarrel; but we should like to point out to the Société that such excessive demands are hardly likely to redound to the advantage of its members, but will probably at the end spell harm to them.

Thanks to our exquisite artificial neroli oil, which may be regarded as in every respect a complete substitute for the genuine article, and of which the sale consequently has increased in an extraordinary manner, a boycott of the Société by the manufacturers would not at all be impossible. Owing to the favourable yield of oil the prices of neroli oil have remained more or less at the level of last year, and we have consequently been able to make a corresponding reduction in our quotations. For the moment business is quiet, and it does not appear as if any changes in the market position were in prospect.

Nutmeg Oil remains unchanged at low prices. There has been no lack of cheap nutmegs suitable for distilling, and occasionally exquisite material could be found at ridiculously low prices. All those interested in the article are advised, when requiring large parcels, to ask us for special quotations.

In order to clear up to some extent the confusion which appears to prevail in commerce as to the derivation of nutmegs, E. M. Holmes[1]) describes the more important species, among which he mentions the following —:

Myristica fragrans Houtt., Banda, or genuine nutmeg. These nutmegs are roundish-ovate, occasionally long nutmegs of a variety of the official species are found mixed with them. We have already previously referred to the constitution of the oil of this species.[2])

[1]) Pharmaceutical Journal **82** (1909), 419 and 459.
[2]) Report April **1908**, 76.

Myristica argentea Warb., Wild, Papua, Macassar, or long nutmeg This species, which is of low price, was formerly an article of commerce from the Malay Peninsula under the name of *Pala Papua*. In the trade in England these nutmegs are known as Long, Wild, or Macassar nutmegs. They are longish-ovate and cylindrical, their aroma being less pleasant than that of the genuine nutmegs, but very persistent.

Myristica fatua Houtt., False nutmeg. This variety should only deserve attention on account of being confused with Papua nutmegs. It has never been a commercial article and differs from the Papua nutmegs in being practically odourless.

Myristica malabarica Lam., Bombay nutmegs. They are occasionally imported. They are longer than the Banda or the Papua nutmegs, and are practically odourless. In the spice-trade they must be regarded as an adulterant of genuine nutmegs.

In connection with the above, we may refer to two new wild nutmegs on which E. Heckel[1]) reports. He received the fruits of *Brochoneura vouri* Warb. (*Myristica vouri* Baill.) from the Province of Farafangana in Madagascar. The natives crush the nuts and press them under the application of heat, thus obtaining a grease which they use as a remedy against scratches and as pomatum for the hair.

The second fruit is derived from a new variety, which Heckel calls *Brochoneura dardaini*. This has an extremely pleasant odour and is used by the natives for similar purposes as *B. vouri*.

Orris Oil. The usual report of our informants this season is as follows: —

"Since we reported last on Florentine orris root, an unexpectedly strong demand has developed, which still continues, and under the influence of which the price of old root has gradually advanced to 72 marks cif Hamburg for sorts and 62 marks for pickings. Speculation has also contributed its share to this rise, because in view of the greatly reduced stocks and the moderate crop-prospects, the opinion prevails that it is more likely that the market will rise than that it will recede. As already frequently mentioned, it is impossible to form a careful estimate of the result of the harvest before November, because the collection of the roots (which, during the later stages, it is true, are often of poor quality), frequently continues until that month; but from what we have ascertained at the various centres of production, it appears that the total output which may be expected is at the very most 500 tons.

The stock at the end of February 1909 was	about 750 tons,
the shipments from end of February to end of August . .	„ 490 „
there thus remain in stock	about 260 tons,
add to this an estimated crop of	„ 500 „
estimate of supply available for the new season beginning 1st September 1909	about 760 tons.

Of the 750 tons which were said to be in store at the end of February 1909, only about 260 tons remain, of which about 120 tons are in the

[1]) Répertoire **21** (1909), 49, through Pharmaceutical Journal **82** (1909), 463.

country districts. The residue of about 140 tons is in the hands of dealers and exporters, and has been partly sold for future delivery. We have frequently referred to a large parcel of about 100 tons of worm-eaten root which was included in the total stock at the time of our report; half of this has in the meantime been bought by a speculator, who appears to have already disposed of it. The first annual markets of Florentine orris were held in the principal producing districts in the first days of August, and were visited by us. The offers were of little importance and the sellers did not scruple to ask prices which are equivalent to from 80 to 85 marks cif Hamburg for sorts. Naturally such demands did not lead to business. In our opinion, when the first excitement is past we will be able to buy sorts at about 74 marks cif Hamburg. The exports from the end of February to the end of August 1909, totalling about 490 tons, together with the exports of the previous half year, amounting to about 265 tons, give a total export for the last business-year of about 755 tons. The annual exports for the last 7 years have been as follows: —

September 1902/August 1903	about 840 tons,
September 1903/August 1904	„ 820 „
September 1904/August 1905	„ 500 „
September 1905/August 1906	„ 920 „
September 1906/August 1907	„ 550 „
September 1907/August 1908	„ 525 „
September 1908/August 1909	„ 755 „
total	about 4910 tons,
equal to an average of	about 701 tons.

If the exports of Florentine orris in the season which is now beginning should reach the same height as those of last year, there would be no stock left at the beginning of the 1910 crop. It is, however, a fact that as compared with previous years the statistical position of the article has undergone a considerable change."

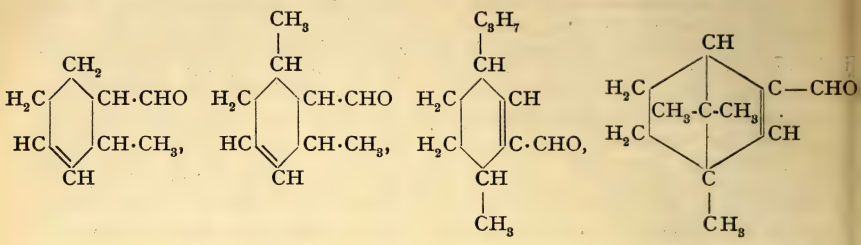
Probably the prices of orris oil in the near future will continue to move within the present range of value.

In an extremely thorough and voluminous paper, G. Merling and R. Welde[1]) report on the synthesis of the odoriferous principles of violets, especially on the natural, or β-irone, to obtain which has required years of difficult research. By far the greater part of the authors' work has been carried out in the laboratories of the Farbwerke, of Hoechst; a small portion of it in our own laboratories. The publication (which is to be followed by others) contains in its introduction a concise account of the process of synthesis of the, as yet unknown, isomerides of α- and β-cyclo-citral (Δ_1- and Δ_2-cyclo-citral), namely Δ_3- and Δ_4-cyclo-citral and their condensation-products with acetone, α- and β- (natural) irone, as well as theoretical considerations on the structure of the molecules of the odoriferous principles of the violet. From the latter it appears that only cyclic aldehydes of very definite structure, such, for instance, as cyclo-citral and its isomerides are suited

[1]) Liebig's Annalen **366** (1909), 119.

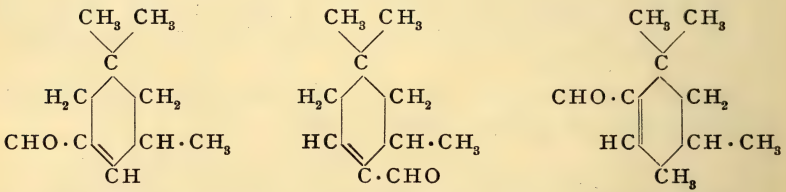
for the preparation of usable odoriferous substances, and especially of violet-perfumes, and that cyclic aldehydes[1]) of the following formulæ: —

I. II. III. IV.



such as are derived from methyl and dimethyl cyclohexenone, menthone, and camphor, do not give sweet-scented condensation products with acetone. Again, in the case of the molecule of cyclo-citral the manner in which the aldehyde group and the side-chains are reciprocally grouped is of importance for the production of a valuable perfume. Thus, for instance, among the aldehydes[2]) of which the positions are isomeric with cyclo-citral, and which are constituted as follows: —

I. II. III.



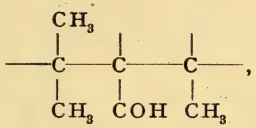
b. p. 85 to 86° (11 mm.) b. p. 73 to 74° (7 mm.) b. p. 101 to 102° (17 mm.)

No. II, and especially No. III yield, with acetone, condensation products (b. p. 130°, 6 mm., or b. p. 132 to 134°, 10 mm.) of a pronounced odour of violets, whereas the condensation product of aldehyde I (b. p. 127 to 128°, 6 mm.) is almost odourless. As regards their quality and the intensity of their odour they are not, however, to be compared with irone and ionone. From the foregoing it must therefore be concluded that the position of the aldehyde groups in the cyclogeraniolene ring has a decisive influence upon the odoriferous properties of the condensation products of acetone. The authors express the law of relationships between the structure and the odour

[1]) German Pat. Nos. 119862, 119879, 121975, 148206, 148207.

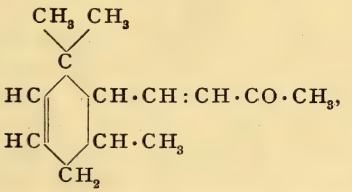
[2]) German Pat. Nos. 119862, 119879, 121975, 136873, 141699, 141973, 142139, 158075.

of the latter as follows: "Aldehydes which are derived from cyclogeraniolene form, with acetone, combinations possessing an odour of violets, insofar as the aldehyde group is adjacent either to the methyl or to the *gem*-dimethyl group, or to both at the same time, and the intensity of the violet-odour increases in proportion to the number of methyl-groups which are adjacent to the aldehyde-groups. The condensation product of acetone loses its characteristics as an odoriferous substance as soon as the aldehyde group is removed from the proximity of the methyls (Aldehyde I)". Merling and Welde have also discovered that isopropyl ethyl acetaldehyde, in which the atoms were grouped as follows:

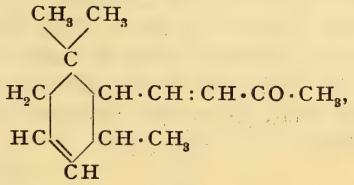


(a grouping which is also found in the cyclogeraniolene ring), was capable of being condensed with acetone to a body possessing an odour which, although agreeable, no longer had the character of a violet-scent.

The synthesis of natural irone, called by the authors β-irone



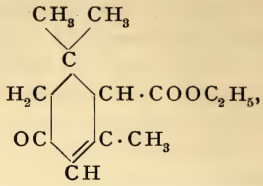
and of its isomeride, α-irone



starts from *iso*propylidene aceto-acetic ester, a yellowish oil, boiling at 70 to 73° (2 to 3 mm.), or at 75 to 78° (6 mm.). This body is obtained by Pauly's[1]) process, slightly modified, which consists of saturating a mixture of 1 part acetone and 2 parts aceto-acetic ester with hydrogen chloride at — 5°. With sodium aceto-acetic ester it

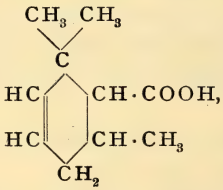
[1]) Berl. Berichte **30** (1897), 482.

condenses to *iso*phorone carboxylic ester[1]) or δ-keto cyclogeraniolene carboxylic acid ester, with the formula



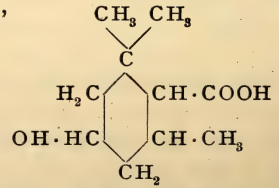
a yellowish oil with a characteristic aromatic odour, b.p. 115 to 120° (4 mm.) or 136 to 140° (10 mm.).

We can here only indicate briefly the further course of the synthesis of β-irone, (which is identical with the natural substance,) because the authors propose to reserve full details of the subject for a subsequent paper. It is based upon the preparation of Δ_4-cyclogeranic acid, which occurs in two stereo-isomerides:



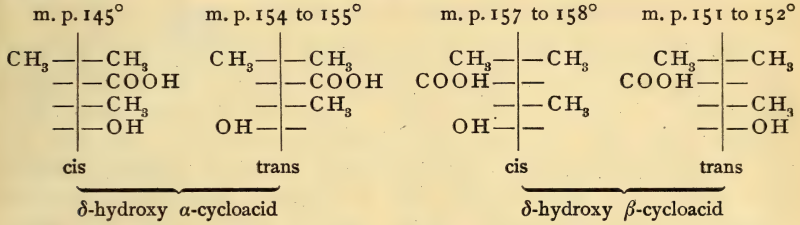
This Δ_4-cyclogeranic acid is obtained, together with Δ_3- and Δ_2-cyclogeranic acid, in the course of the decomposition of δ-chlorocyclogeranioladienecarboxylic acid[2]) one of the products of reaction of phosphorus pentachloride with *iso*phorone carboxylic ester. According to a process of which details have already been given by Merling[3]) this acid is converted *via* the acid chloride, the acid anilide, the phenylimide chloride, the diphenyl amidine and the diphenylmethylenediamine into the corresponding aldehyde, Δ_4-cyclo-citral. This, when condensed with acetone by the familiar process, yields β-irone.

When *iso*phorone carboxylic ester is reduced with sodium and alcohol, the result is a mixture of two pairs of stereo-isomeric δ-dihydroxy-cyclogeranic acids, (δ-hydroxy-cyclogeraniolanecarboxylic acids) Germ. Pat. No. 148207,



[1]) Germ. Pat. No. 148080. See also Berl. Berichte **38** (1905), 979.
[2]) Germ. Pat. No. 175587.
[3]) Berl. Berichte **41** (1908), 2064; Report November **1908**, 183.

with two isomeric γ-hydroxy*iso*propyl methyl cyclopentane carboxylic acids (?). The authors have very thoroughly investigated the complicated relationships which exist between the first four acids, and they treat at great length of their properties, their chemical behaviour, their convertibility one into the other and their separation. It would carry us too far to explain all these phases here, and it may suffice to point out that these acids represent *cis-trans*-δ-hydroxy α-cyclo- and *cis-trans*-δ-hydroxy β-cyclogeraniolane carboxylic acids of the following composition[1]): —



Among these, the *trans*-α and the *cis*-β-acids are very prone to give off water and thus to become converted into the two stereoisomeric Δ_3-cyclogeranic acids[2]). On the other hand, the two remaining acids energetically resist dehydrating agents. The conversion of Δ_3-cyclogeranic acid into Δ_3-cyclocitral takes place by the method indicated above for Δ_4-cyclocitral. With acetone the aldehyde yields a condensation product of an odour somewhat reminding of irone, which the authors therefore call α-irone. Detailed particulars as to the properties of the two perfumes, α- and β-irone, as well as of the bodies from which they are built up, the cyclogeranic acids, cyclocitrals and their intermediary compounds shall be given in the next paper.

Palmarosa Oil. In anticipation of the crop which is now beginning to be gathered, prices have given way by about 10%, but much more liberal offers are required in order to bring the quotations below 6/-. In the meantime there are very few firm offers.

According to cable report which has recently been received, the monsoon is said to have been unfavourable and to have adversely affected the new crop. .

We are again indebted to the kindness of Mr. J. H. Burkill, of the Indian Museum, at Calcutta, for a description founded upon his own observations of the manner in which "rusa oil" is obtained in the district

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[1]) The designations *cis* and *trans* refer to the reciprocal positions of carboxyl and hydroxyl.

[2]) Germ. Pat. No. 148206.

of Amraoti. We tender Mr. Burkill our most sincere thanks for sending us this report, which forms a welcome supplement to previous notices.[1]) A number of photographs and sketches accompanied Mr. Burkill's letter and out of these we have chosen one representing a distilling plant to illustrate this Report (see frontispiece); sketches of the apparatus used in distilling and of the receivers will be found in the report of Mr. Burkill, the text of which we subjoin.

Distillation of Rusa or Palmarosa Oil in the District of Amraoti, Province of Berar, India.

The oil distilling industry about Ellichpur is worked in the following way. The forest lands where *Cymbopogon Martini* var. *Motia* grows are leased out to men of substance — generally Mohammedans, who for the most part sub-lease them again piece-meal to men who go out to selected valleys in the Melghat with stills and engaging villagers send some out to cut the grass tops at so much per hundred bundles brought in, and with others set up open-air distilleries on the banks of the streams. There is built first a row of stone fire-places and the cauldrons are set up on them, generally 3 or 4 in a row. The cauldrons are sometimes of iron and sometimes of copper. If they are of copper they are generally somewhat smaller than those of iron and depressed globose; the iron cauldrons are cylindrical and rivetted; they are about $2^1/_2$ feet in diameter. The top of the iron cauldrons is slightly conical with a central lid. Out of the lid emerges the bamboo elbowed tube by which the distillate passes off.

The cauldron once set in place ready for the fire, is never moved.

The elbowed tube has a bamboo peg run through it at the angle and is wrapped from end to end in string. From the elbow the longer part is about six feet.

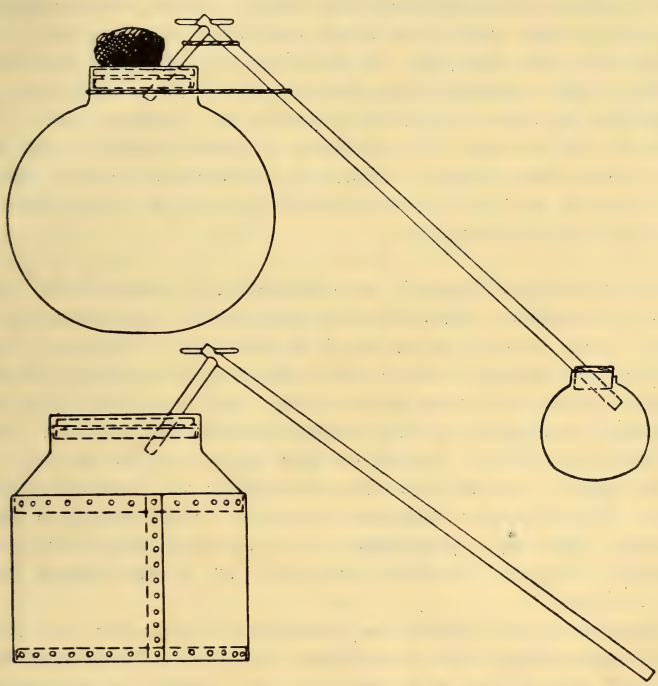
The receivers are generally long necked, more than a foot in diameter below, not so deep as broad (neck excluded). But sometimes they are without a neck, in which case a pad of cloth on the bamboo closes the mouth. They are generally made of copper. They are placed in the water quite up to the neck. A framework of wood lies in the stream which is generally dammed to deepen the water. Into the interspaces of this framework the receivers fit, being held in place by means of two sticks of wood which are tied on either side of the neck and are placed under the cross bars of the framework. Further, stones are heaped round each receiver to help to keep them under water.

The method of work is as follows. We will suppose that the cauldron has just been emptied of a charge and lies with the lid off and with the fire drawn from below it. A workman standing on the

[1]) Gildemeister and Hoffmann, *The Volatile Oils*, p. 282.

stone walls round the cauldron, with a rod measures the depth of the water in it. This water is brown and holds a considerable amount of tannin derived from previous charges of grass. Next he pours enough clean water into the cauldron to bring the depth up to about (for a large cauldron) 10—12 inches and next packs in the grass often trampling it down in order to get as much as possible in.

The stills are of different sizes. The larger one takes a charge of about 200 bundles of grass (each bundle containing about 300



stems) and the smaller takes about half the quantity. Next the lid is replaced and the joint luted up with a paste of flour of udid (*Phaseolus*) and a muddy bandage. The bamboo tube is inserted into the hole in the lid where it fits and is similarly luted in. Next, fire is put under the cauldron and boiling recommences.

The boiling lasts two or three hours; and according to the arrangements which the masters make with the men, five or six boilings are done in the twenty-four hours.

The bamboo passes into the receiver for a distance of about six inches. After a while the bubbling of the steam through the increasing

distillate begins to give what the workmen describe as the sound "tit-tit". The sound deepens and when it becomes what they call "bul-bul" they know to stop the boiling. In doing this the fire is removed, cold water thrown over the lid of the cauldron, the bamboo tube removed, the lid lifted, and the receiver taken out of the stream. The pressure of the steam in the cauldron is at this time not inconsiderable.

While some men with a hay-fork are removing the exhausted grass from the cauldron, the master takes with a spoon the oil from off the top of the water in the receiver and using a funnel of tin he separates it from any water which the spoon brings up with the oil.

In some stills lime juice is used now to help to clarify the oil.

Three large cauldrons give about a pint and a half of oil, which on standing deposits a sediment generally of a copper salt.

All the oil of each small distillery is mixed together and carried to the nearest trade centre — Ellichpur, for most of the stills examined.

Table salt to the extent of half a pound is thrown into each cauldron every few days.

In our previous Report[1]) we published the results of the examination of 8 samples of palmarosa oil and one of gingergrass oil, which had also been sent to us by Mr. J. H. Burkill, of Calcutta. The oils are of special interest because they had been collected by Mr. Burkill during a journey of investigation through the producing districts, and had partly been taken by him personally from the receivers. He has now published further notes[2]) on the results of his journey, which contains much that is of interest, and which we therefore reproduce briefly. The publication includes a note on the differentiation between palmarosa grass and gingergrass — a question which has already frequently occupied botanists, but which up to the present has not been elucidated[3]).

Palmarosa grass (Motia) and gingergrass (Sofia) are, according to Burkill's observations, doubtless different varieties of *Cymbopogon Martini* Stapf, and in his view it is therefore quite correct to designate them directly as var. *Motia* and var. *Sofia*.

It is however not easy to distinguish them from each other, as on the whole they are very much alike and their chief difference is a chemical one, the oils contained in them being different. It is practically impossible to notice any differences in dried specimens of the grass, for which reason even so experienced a botanist as Stapf

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[1]) Report April **1909**, 56.

[2]) J. H. Burkill, First Notes on *Cymbopogon Martini* Stapf. Journal of the Asiatic Society of Bengal, March 1909, Vol. V, No. 3 (N. S.) From a copy kindly sent to us.

[3]) Comp. Report April **1907**, 35, 57.

was unable to recognise any variation in the two grasses. The subject is placed in quite a different light, however, when the grasses are seen in the open in the place where they grow. Here they are soon differentiated by their external appearance, and after a time they can be distinguished even at a distance of 15 to 20 yards. The reason of this is that the grasses do not grow equally well in the same localities, as each requires a different climate and soil. As a result, when they grow side by side and under the same conditions they develop unequally, which makes it possible to distinguish them without difficulty.

Burkill found that Motia flourishes best on dry soil at the foot of the hills or on moderately high slopes facing southwards and only slightly wooded. Sofia, on the other hand, demands moisture and grows particularly well where this is supplied by plentiful dew or mist. It prefers higher altitudes and wooded places, even as high as the hill tops, but it may also be found at lower slopes, except those which face southward. Very favourable places for Sofia are the teak forests (*Tectona grandis* L., East-Indian Oak) where, owing to the rapid evaporation of water during thenight, the air cools down to a considerable degree, and abundant dew is formed. But in spite of all these individual preferences, both Motia and Sofia may be found at any altitude, provided the other conditions are favourable.

With regard to the distribution of the two grasses in different neighbourhoods, Burkill was able to determine that Motia and Sofia both occur, although at different altitudes, near Asirgarh, Chandni, and in the Melghat, while in Deogaon and Belkhera, to the West and North-East of Ellichpur — an important commercial centre for palmarosa oil — as well as in Dhamangaon, he found almost exclusively Motia, Sofia only gradually occuring in larger quantities as he came further into the mountains. But beyond the water-shed in the valley of the Sipna up to the Tapti River he found only Sofia.

The differences between Motia and Sofia vary according to the district in proportion as the conditions of development are more favourable to one or the other of the plants. For this reason the descriptions given by the grass collectors do not agree. For example, in the district of Asirgarh and Chandni, Motia grows straighter and higher (6 to 8 ft.) than Sofia (3 to 4 ft.), and the latter also has dense and bushy tops; but in the Melghat, Sofia is the larger of the two plants. The width of the leaves and the intensity of the colour increases with the height. Sofia is characterised by the fact that it sends out numerous runners, which Motia does not. It also appears that the angle formed between the leaf and the stalk is different in the two varieties. Another interesting observation of Burkill's is that in various places he noticed grasses which were neither Motia nor Sofia, and which he regards as hybrid forms. He considers it prema-

ture, however, to make any final pronouncement on this subject until the whole subject of *C. Martini* — of which presumably still other varieties are extant — has been cleared up.

It is also interesting to refer to the etymology of the words Motia and Sofia. The former means "like a pearl" — that is to say, valuable; the latter means "small" — or "of slight value". It is Burkill's intention to continue his studies on these grasses.

Patchouli Oil. In our last November Report[1]) we gave particulars of investigations made by de Jong at Buitenzorg on Singapore patchouli leaves for the purpose of obtaining more accurate information as to the oil-content of the leaves in different stages of development. More recently de Jong has made similar investigations with Java patchouli leaves.[2]) The latter investigations led to results similar to those obtained with Singapore leaves; the oil-content increases up to the third pair of leaves counting from the top of the branch, and then gradually decreases.

The comparative distillations which de Jong has carried out on the present occasion with material which had been submitted to various kinds of preliminary treatment are of particular interest. Both Java and Singapore leaves were employed. In one experiment de Jong used quite fresh leaves; in another dried leaves; in a third fermented leaves; the quantity being the same in every case, calculated for green material. The stalks had been removed before the experiment, as they contain only little oil. The leaves were dried in shady places, being spread out in a layer 5 cm. high, which was turned over daily until the leaves were quite dry and brittle. For the purpose of fermentation de Jong first half-dried the leaves and then placed them on layers forming a heap, which was covered with bamboo matting (*Tetampa*), weighed down with stones. The leaves were mixed together every day in order that the fermentation might proceed as uniformly as possible. The process was continued until the temperature inside the mass of leaves did not exceed that of the surrounding atmosphere. According to the degree of moisture of the leaves the maximum temperature observed was from 35 to 52°. A mouldy odour was usually observed, but this was removed by spreading out the leaves at the end of the fermentation process and only distilling them a few days later.

The distillation was carried out by steam (3 to 4 atmospheres). In every case the leaves, after being distilled, were freed from water by pressure, dried, and again distilled. The quantity of oil obtained from green leaves was very much smaller than that from dried and

[1]) Report November **1908**, 95.
[2]) Teysmannia **1909**. From a copy kindly sent to us.

fermented leaves. The following table, showing the yield obtained by de Jong from Java leaves, is of interest:

Condition of the leaves	Quantities worked, calculated for green material	1st distillate	2nd distillate	Total distillate
Fresh	70 kg.	38 cc.	114 cc.	152 cc.
Fermented	70 „	375 „	30 „	405 „
Dried	70 „	360 „	49 „	409 „
Dried	70 „	315 „	69 „	384 „
Fermented	70 „	350 „	28 „	378 „
Fermented	70 „	359 „	28 „	387 „

From the above it is clear that it is quite useless to work up green leaves, because they only yield very little oil, and even in this case the principal quantity was obtained from the second distillation, that is to say, after the leaves had been dried. Much more considerable outputs, on the other hand, are obtained from dried and fermented leaves, almost the total oil contained in them being yielded by the first distillation, the second producing comparatively little oil. The total quantity of oil in dried and fermented leaves is about the same.

As regards Singapore leaves, similar conditions prevail. In the case of a single distillation, 24 kilos of the leaves in a green state produced 20 cc. oil, but after drying they yielded 77 cc., and after fermentation 86 cc. The small yield of Singapore as compared with Java leaves is due to the fact that in the former case the distillation took place at atmospheric pressure only.

The great differences in the oil-yield between green leaves on the one hand and dried or fermented leaves on the other, may be traced to the circumstance that the oil cells are placed partly on the surface and partly inside the leaf, and that when fresh leaves are distilled almost the only cells from which the oil is liberated are those on the surface. The fading of the leaves which occurs during the drying or fermentation process, renders the cell-membranes more porous, so that the oil contained inside the leaf also can be separated out by distillation. No oil is formed during the drying or fermentation, and the proof of this — so far as fermentation is concerned — is that the dried leaf yields the same quantity of oil as the fermented leaf.

The fact that when green material is used the oil-yield is increased in proportion to the steam-pressure and becomes very considerably greater when superheated steam is used, is in conformity with these views. De Jong's explanation of this is that the rise in temperature brought about by the increase of the steam-pressure causes destruction of further cells, resulting in the liberation of more oil. He also proved by experiments that the yield of oil may be greatly increased by

cutting up the green leaves before distilling them. This, however, was not due to any enzyme action, because de Jong obtained the same results with leaves which had been previously steeped in boiling water.

De Jong intends to continue his studies into the processes described above.

De Jong has sent us samples of the oils obtained in the course of his experiments, and the examination of these was described by us some months ago [1]).

In an inaugural dissertation, Fritz Mayer [2]) deals with the systematic-anatomical investigation of the *Pogostemoneæ* Reichenb. He refers in particular to the internal glands of which the structure agrees with that of the external bladder-like glands of the skin. The author found these glands to exist in all species of *Pogostemon* and *Dysophylla*. It appears that the secretion of both the external and internal glands (which occur in the leaves, branches and roots, but not in the organs of reproduction, such as flowers, fruit, and seed) is identical. After discussing in detail the stages of development of the internal glands and the structure of the leaves, Mayer communicates the results obtained by him in the course of the examination of patchouli (the drug). Judging by the exomorphous conditions of the leaves, and considering their anatomical characteristics, it is quite possible that all the drugs examined were derived from the same species of *Pogostemon* [3]). The morphological conditions and the structure of the leaves of the drugs are described at length. As adulterants of patchouli Mayer mentions *Urena lobata* L. and *Ocimum Basilicum* L. var. *pilosum* Benth. the anatomical and morphological conditions of which he describes in detail.

Pennyroyal Oil. It appears that the scarcity of this oil, which has so long prevailed, is now at an end, sufficient quantities being offered both from Spain and Algeria at advantageous prices. In the course of the next few months the quotations may recede further, the demand being not at all brisk.

Peppermint Oil, American. We are in receipt of a lengthy report on the American peppermint districts from our New York branch, which this season also has obtained its data by despatching a special representative to Wayne County, Michigan and Indiana.

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[1]) Report November **1908**, 96.

[2]) From a copy kindly sent to us of the dissertation: Systematisch-anatomische Untersuchung der *Pogostemoneae* Reichenb., unter besonderer Berücksichtigung der inneren Drüsen von *Pogostemon* und *Dysophylla* sowie der Patschuli-Droge. Erlangen 1909.

[3]) For *Pogostemon* see Report April **1908**, 80; November **1908**, 95

I. Wayne County, New York.

The peppermint-growing area this year, as last year, lies in the districts of Arcadia, Lyons, Sodus, Marion, and Palmyra, and there has been no change whatever in the economic conditions since 1908. Owing to the low prices ($ 1.40 per lb.) everybody is becoming completely discouraged with the cultivation of the plant, and whereas in 1908 a total area of 379 acres was under cultivation, it has been restricted this season to only 278½ acres. Peppermint-growing, therefore, will gradually disappear entirely from this neighbourhood. This year also a quantity of about 25000 lbs. of peppermint oil remains unsold in the hands of the producers, who are awaiting better prices, and are in no circumstances prepared to sell at the present quotations. The average result of this season's distillation is estimated at 30 lbs. per acre for the newly planted, and 10 lbs. per acre for the old fields.

The following figures give particulars of the cultivation: —

	this year		last year	
Williamson	2	acres	2	acres
Marion	19½	„	13½	„
Palmyra	11	„	14	„
Sodus	18½	„	15½	„
Arcadia	49½	„	46½	„
Junius	6	„	3	„
Galen	4	„	8	„
Lyons	34	„	31½	„
	144½	acres	134	acres.

It is true, therefore, that more peppermint has been planted this year than in 1908, when the new cultivations only amounted to 121½ acres, but notwithstanding this the total area, as stated above, has decreased.

The total output of the Wayne County peppermint plantations during the present year is estimated as follows: —

144½ acres of this year's plants, at 20 lbs. p. acre, abt. 4335 lbs.
134 „ of last „ „ „ 10 „ „ „ „ 1340 „
Total about 5675 lbs.
Add old stock in producers' hands . . . . . 25000 „
Total available for 1909 . . . . . about 30675 lbs.

II. Michigan and Indiana.

As will be seen from the figures given below, the area planted with peppermint in these two States has been reduced by about 4000 acres, but this great reduction is more than counterbalanced by the large quantities of oil which are still in the hands of the farmers. The scarcity of new plantations is especially striking. If this year

again no better prices should be obtained, the interest will be further paralysed. The yield of oil this season is described as unfavourable, and as, owing to the bad climatic conditions the plants have not developed particularly well, distilling was delayed until the end of August so as to give the plantations the longest possible time for further development.

	1908	1909 this year's	1909 total	Oil of 1908 in farmers' hands
a) Michigan.				
Allegan Co. . .	2194 acres	348 acres	1856 acres	23000 lbs.
Cass Co. . . .	1656 „	474 „	1348 „	11000 „
Van Buren Co. .	1592 „	203 „	1295 „	10000 „
St. Joseph Co. .	649 „	195 „	356 „	10000 „
Berrien Co. . .	616 „	140 „	353 „	32000 „
Eaton Co. . .	550 „	205 „	620 „	6000 „
Kalamazoo Co. .	420 „	128 „	294 „	12000 „
Branch Co. . .	290 „	95 „	189 „	7000 „
Muskegon Co. .	172 „	29 „	111 „	1500 „
Total	8339 acres	1817 acres	6422 acres	112500 lbs.
b) Indiana.				
La Grange Co. .	1500 acres	30 acres	530 acres	2000 lbs.
Noble Co . .	818 „	100 „	390 „	3000 „
Steuben Co. . .	400 „	55 „	155 „	5000 „
St. Joseph Co. .	1400 „	330 „	1060 „	8000 „
Total	4118 acres	515 acres	2135 acres	18000 lbs.

Altogether, therefore, there are this year 8557 acres under peppermint-cultivation in Michigan and Indiana, of which 2332 are new plantations. The stock of old oil is estimated at not less than 130500 lbs. In order to explain the not inconsiderable difference between the figures given above for 1908 and the statements made in our November Report of last year[1]), we desire to point out that last year's estimates could only be completed and corrected as time went on. Anyone who knows the difficulties connected with the compilation of such statistics on the spot will immediately admit the possibility of such divergencies.

It is quite evident from these two reports that there will be no scarcity of American peppermint oil during the coming season, and that very strong exterior influence would be required in order to drive the prices to a higher level. In America the general opinion is that in the course of the present autumn the value will advance,

[1]) Report November **1908**, 98.

but we are unable to support this view, as it does not appear to us that there is any logical reason for it.

The exports of peppermint oil from the United States in the course of the last 3 fiscal years (July to June) were as follows: —

1906/7	147722 lbs.,	value	$ 499082.—
1907/8	141617 „	„	„ 357555.—
1908/9	160811 „	„	„ 288318.—

These statistics show that the exports in the course of the last 3 years have advanced 10% in quantity, whereas their value has receded by about 50%.

The shipments during the first six months of the last two years were as follows: —

	1909		1908
January	10515 lbs.		12611 lbs.
February	9250 „		11449 „
March	11961 „		15536 „
April	6461 „		9475 „
May	6560 „		8678 „
June	9822 „		7648 „
Total	54669 lbs.	against	65397 lbs.

Contrary to the state of things disclosed in the above statistics, the sale of our popular brand of rectified American peppermint oil "F. S. & Co." during the past few months has been more animated than in 1908; in fact the sales exceeded considerably those which were made in the corresponding period of the record year 1907. Consumers appear to be gradually adopting the view which we have so long expressed, that the employment of a quality of such excellence as the one referred to above produces far better results than can be obtained with the "cheap" Mitcham peppermint oils which are being plentifully offered, but which are dear at any price.

Peppermint Oil, English. When the present report went to press, the 1909 crop, — which of course has been considerably belated —, was not yet concluded, and its results can therefore be estimated only approximately. It is natural that the high prices which have ruled during the last few years have again led many planters to interest themselves in the article, and that therefore in some of the Northern districts considerably more land was laid under peppermint this year than in 1908. However, during the growing time of the plants there has been a want of sunshine, as a result of which the oil-cells have been unable to develop sufficiently, and therefore, notwithstanding the increased area cultivated, no greater output of oil can be expected this year than last, so that very probably the prices

will remain at their present level. At the moment, pure crude oil is quoted in England at 30/- to 31/- per lb. It is notorious that great caution must be exercised in purchasing, Mitcham peppermint oil being an article of confidence in the most literal sense of the term.

Peppermint Oil, French. Roure-Bertrand Fils[1]) in the last issue of their report, give further particulars of the progress of their investigations of French peppermint oil[2]). By fractional distillation of the oil, which had previously been saponified, they were able to isolate and identify the following constituents: — 1. Isovaleric aldehyde. 2. Isoamylic alcohol. 3. l-Pinene. 4. Δ^3-p-Menthene(?). 5. Cineol. These constituents amount to about 6% of the oil examined. Analysis also showed the oil to contain 38% of free and 13,5% of esterified menthol, as well as 6,4% of menthone. Further details as to the investigation, which is still proceeding, are promised.

Peppermint Oil, Japanese. The firmer tendency of the Japanese peppermint oil market during the months of March and April was supported about the middle of May by the news that in Hokkaido, in the province of Kitami, in the neighbourhood of Yubetsu, Takoro, and Natsukenshi, large tracts of the cultivations had been destroyed by floods, the damage at that time being estimated at from 30 to 40% of the total. Owing to a brisker demand from the United States, prices gradually advanced to 9/2 for menthol and 5/9 for oil, but at these quotations no transactions took place, the market movement gradually becoming flatter, and falling to 8/- for menthol and 5/5 d. for oil. The tendency in the European market may be gathered from the fact that both articles were repeatedly quoted in London at lower prices than in Japan.

This year's output of peppermint oil in Japan is estimated at about 110000 kin, of which 100000 kin will be produced in Hokkaido. In some quarters the estimates as regards Hondo are given at even lower figures than those supplied by our informants. It is hardly likely that the new crop will be on the market before the end of the year. The old stocks still in the hands of the farmers and refiners are estimated at about 100000 kin, which, compared with former years, must be regarded as very small. When we consider that Hokkaido peppermint oil is notoriously poorer in menthol than is Hondo oil, it will be seen from the above figures that, especially as regards menthol, the market may be described as firm. It is pretty certain therefore that there will be no fall in prices of this product during the coming season, while, on the other hand, the Japanese of course will

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[1]) Berichte of Roure-Bertrand Fils, April **1909**, 40.
[2]) Comp. Report April **1909**, 76.

do their very utmost to exploit the position and to obtain higher rates for their products.

For the map of the Japanese peppermint districts which will be found in this Report (facing back cover) we are indebted to the courtesy of Messrs. M. Raspe & Co., of Kobe. In comparing this map with the one published in our Report for April 1897, it is to be considered that in the present map the coloured districts show the actual areas under cultivation, whereas in that of 1897 the entire provinces where peppermint oil was grown were coloured, even although only a small part of them might be under peppermint cultivation. The letters printed in the various districts of the present map refer to the following estimate of the 1909 crop: —

A (Yamato)		100 kin
B (Bingo-Bitchiu and Bizen)		8 500 „
C (Sanuki)		200 „
E (Ishikari, Teshio and Tokachi)	(Hokkaido)	20 000 „
H (Kitami)	(Hokkaido)	80 000 „
N (Shinano)		300 „
Y (Uzen)		500 „
		109 600 kin
	equalling in round figures	65 900 kg.

A British Consular Report from Northern Formosa[1]) indicates that the growing of peppermint has recently been taken up successfully in Formosa at Bokuseki-kaku in the district of Tuito, near the east coast of the island. In the first year (1908) the crop was cut 3 times, the first cutting yielding 990, the second 3200, and the third 2310 lbs., together 6500 lbs. of herb. This, is is true, is only equal to an oil-output of about 105 lbs., but in any case it may be taken for granted that in future a keener interest will be shown for this cultivation, which according to the statements of the Consul is said to yield a profit of £ 11 to £ 12 per acre.

Peppermint Oil, Saxon. Unfavourable weather has unfortunately greatly injured our peppermint cultivations, so that a satisfactory result is again out of the question. The second cutting, which is just about to begin, promises better results than the first, but is hardly likely to make good the loss already existing. In any case no reduction is to be expected in our prices during the coming season, and our supplies will soon be reduced — in fact, an advance in our prices would actually be justified.

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[1]) Diplomatic and Consular Reports, No. 4240, June 1909.

As it is possible to introduce the cultivation of peppermint to advantage in many British Colonies, the *Bulletin of the Imperial Institute*[1]) publishes for general information a review on the cultivation of the peppermint plant and the production of the oil in the various countries concerned.

As is well known, the largest quantities of peppermint oil are produced in the United States, Japan, France and England, smaller quantities being also obtained in Germany, Italy and Russia. The oil distilled in America and Europe is derived from varieties of *Mentha piperita*, while the Japanese oil is obtained from *Mentha arvensis*. Two varieties of peppermint are specially known, the so-called "black mint" (*Mentha piperita* var. *vulgaris*) and the "white mint" (*Mentha piperita* var. *officinalis*). The first-named is the hardier and produces a larger proportion of oil; the latter yields less oil but of finer quality.

In the United States, peppermint plantations have been laid down in the States of New York, Indiana, but principally in Michigan. According to its condition the soil, after the second crop, is either sown for 5 years successively with clover, corn or other produce, before being again laid under peppermint; or the peppermint is allowed to grow 6 or 7 years in succession on the same soil, the land being ploughed up after every crop and the succeeding years' plants being grown from runners.

The roots, which are used for planting, are from $^1/_8$ to $^1/_4$ in. thick and 1 to 3 ft. long, and are laid in the prepared soil in furrows at distances of 3 ft., forming long separate lines. An expert workman can plant about one acre a day. Within about a fortnight the plants begin to show aboveground, and the land is then carefully hoed and cultivated until, in Juli and August, the runners which have developed make further cultivating difficult. If towards the end of the season the weather turns very wet the plants are apt to be attacked by what is known as "rust", which causes the leaves to drop off. It is necessary to keep the ground free from weeds, as any weeds with a strong odour, when gathered along with the peppermint, may injuriously affect the quality of the oil. The harvest begins in the second half of August, when the plants are in full flower, and lasts until the middle of September. Distilling continues day and night until everything is worked up. The highest yield and the best quality of oil are obtained from the first year's cutting. The oil-yield from the same field varies considerably, the atmospheric conditions prevailing during the harvest apparently influencing it. Mint cut after a warm and humid night gives more oil than that cut after a cool dry night.

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[1]) Bull. Imp. Inst. 7 (1909), 184.

After cutting, the peppermint is slightly dried, but not to such an extent that the leaves fall off, and is then distilled as quickly as possible. Some operators distil the plants in the green state, as they fear that drying will cause loss of oil. About 330 lbs. of dried peppermint yield 1 lb. of oil; the output per acre equals from 12 to 50 lbs. of oil.

Various kinds of distilling apparatus are in use, but they all consist of a boiler, 2 wooden vats, a condenser and a receiver. The vats are used for receiving the herb and are alternately filled and emptied. They are 6 ft. high, with a diameter of 5 ft. A steam-tube leads from the boiler through the bottom of each vat, so that the steam passes through the distilling material from below. In large distilling plants the vats contain 2000 to 3000 lbs. of dried herb.

According to the *Journal of the Board of Agriculture*[1]), from 500 to 1000 acres are under peppermint in England. In this country black mint yields twice as much oil as does white mint, and as a result the cultivation of the latter has been supplanted to a considerable extent. Peppermint grows best at a height not exceeding 200 ft. The principal production is in the districts of Ewell, Cheam, Carshalton, and Mitcham; smaller quantities are also obtained in certain parts of Sussex, Kent, Hertfordshire, and Lincolnshire. In England also the plants are grown from roots, not from seed. The land having been ploughed and manured during the winter, the plants are dibbled in in May. A plantation lasts from 4 to 5 years, the best output being in the second year. After 4 or 5 years the land is not used again for mint growing for some years.

The harvest begins early in September, when a red rust or "snuff" appears on the leaves. After some slight drying the plants are distilled for about six hours. The oil-yield per acre ranges from 8 up to 25 lbs.

The particulars following, relating to the production in Japan contained in the *Bulletin*, are taken from the article on Japanese Peppermint by Naojiro Inouye which appeared in our Report of November **1908**, p. 199.

Petitgrain Oil, Paraguay. Business in this article has been unusually quiet. On the one side the offers were not particularly liberal, but on the other the demand was also halting, and even the present prices, although extremely advantageous, call forth very little interest. The fact that according to the report of the German Consulate in Asuncion the exports were as follows

	1908	30274 kilos
against	1907	10872 „
and	1906	9698 „

[1]) Journ. of the Bd. of Agric. **15** (1908), No. 5.

shows that the difficulties connected with the manufacture no longer appear to be of such a severe character as formerly. The exports, according to the above figures, have more than doubled in the course of the last 2 years. The quality of the present season's arrivals has been unimpeachable throughout.

Pine Needle Oils. In our criticisms of Pharmacopœias[1]) we have repeatedly pointed out that the requirements relating to the boiling points of the oils are without any value unless accompanied by the most precise indications as to the mode of execution of the process, as the determinations are mostly wrongly conducted and result in useless correspondence between manufacturers and pharmacists. Only recently another such case came under our notice, in which a pine needle oil supplied by us to a firm in England was being objected to because its behaviour on boiling was alleged to be improper. The analyst concerned had discovered that the oil contained over 10% of fractions boiling below 165° and consequently did not conform to the requirements of the British Pharmacopœia, according to which not more than 10% may pass over below 165°. A check-test made in our laboratory showed that the objection was completely groundless. The oil proved to be an altogether normal distillate, which in its boiling conditions also conformed with the British Pharmacopœia, inasmuch as it only began to boil at 168°. The reason for the objection raised was therefore to be sought entirely in the inaccurate manner in which the boiling-point determination had been conducted. Unfortunately such instances are very common, and it is therefore earnestly to be desired that in all Pharmacopœias the mode of carrying-out boiling-point determinations should be very carefully described in order to avoid such trouble. *The shape and the size of the boiling flask and the course of the distillation should be specified with exactness, and above all, stress should be laid on the fact that the entire mercury thread in the thermometer must be surrounded by the steam of the liquid.* Only where this is done proper results can be obtained and unfounded claims avoided.

In a fraction of Siberian pine-needle oil with b. p. 240 to 280°, Wallach and Grosse[2]) discovered a sesquiterpene $C_{15}H_{24}$ which readily yielded an easily crystallising hydrochloride. In order to isolate this compound, the oil was boiled for about an hour with concentrated potash liquor and the portion boiling between 250 and 270° saturated in a glacial acetic acid solution with hydrochloric acid gas. The resultant tri-hydrochloride had m. p. 79 to 80°. The hydrocarbon, regenerated by heating with sodium acetate and glacial acetic acid,

[1]) See Report April **1908**, 128, 135; April **1909**, 100.
[2]) Liebig's Annalen **368** (1909), 19.

possessed the following properties: b. p. 260 to 268°, $d_{20°}$ 0,8725, $n_{D\,20°}$ 1,4903, mol. refr. found 67,63, calc. for $C_{15}H_{24}/_3$ 67,86. With hydrochloric acid, the reconstituted hydrocarbon again yielded the trihydrochloride, m.p. 79 to 80°. With hydrobromic acid the corresponding compound of m.p. 84° is formed.

The molecular refraction and the absorbent powers of the hydrocarbon point to its possessing three ethylenelinkings. It is true that this assumption is apparently contradicted by the fact that the sesquiterpene only absorbs four atoms of bromine (with immediate discolouration) but this behaviour may be explained by the presence of conjugated double-linkings.

These results warrant the conclusion that the sesquiterpene of pine-needle oil is identical with that of oil of limette[1]) and oil of opoponax[2]).

In the course of our examination of oil of lemon[3]) we have also occupied ourselves in some detail with this sesquiterpene, and we were able to show that the sesquiterpenes of oils of bergamot, camphor, lemon, limette and opoponax and that of oil from *Piper Volkensii* C. D. C. are identical with the bisabolene already discovered in 1897 by Tucholka in Bisabol Myrrh.

Oil from the Leaves of Ribes nigrum. We have already on a previous occasion[4]) reported on an oil from the buds of the black currant, *Ribes nigrum* L. (Saxifragaceæ), as well as on the bodies which are contained in the leaves of this plant[5]). A communication has now been published by Huchard[6]) concerning an essential oil distilled from the leaves. By the process of decomposition this oil yields quinic acid, also a very active oxydase; a new and most remarkable occurrence in the case of an essential oil. No constants or other properties are recorded, but we are informed that the oil is said to have a diuretic action.

Rose Oil, Bulgarian. The advantageous weather which prevailed during the months of March and April has resulted in the normal development of the flowers, in consequence of which the expectations which were entertained of this year's crop have been realised in every respect. According to the reports to hand, a total of about 4319 kilos has been produced, and although this result does not come up to that of the record crop of 1903 (6250 kilos), it may yet be

[1]) Burgess and Page, Journ. chem. Soc. **85** (1904), 414; Report October **1904**, 54.
[2]) Report October **1904**, 67.
[3]) Gildemeister and Müller: Beiträge zur Kenntnis des Citronenöles (Wallach Jubilee-publication, Göttingen 1909). Comp. p. 62 of this Report.
[4]) Report April **1907**, 106.
[5]) Report April **1906**, 107.
[6]) Journal des Practiciens; through The Practitioner **1909**, 428. From the Pharmaceutical Journal **82** (1909), 528.

regarded as a very favourable one when compared with the crop of 1908, which was only 2652 kilos.

In consequence of this result the prices have gone back by about 10 %, and they would certainly be lower still if special conditions had not imparted to the market a comparatively firm appearance, at any rate for the present. These conditions were that in the course of the spring a rumour went round that in revising the American Customs Tariff it was intended to take rose oil out of the „Free List" and to place upon it, in common with most other essential oils, a duty of 25 %. A number of traders were induced by these reports to ship considerable quantities of last year's oil, the cost of which was comparatively high, to the United States, so as not to miss the profit which was counted upon in case a duty should be decided upon. This speculation has proved a failure, for the few alterations which were made in the Customs Tariff so far as our articles are concerned, have not in any way affected rose oil. The large and costly stocks which are now stored in the U. S. A. are inducing the Bulgarian owners to do everything in their power in order to force up the prices, or at any rate to maintain them at a sufficient level to enable them to get out of their adventure with the smallest possible loss. In view of the abundant result of the new crop it does not appear to us that these efforts are likely to be very successful, and the firms referred to, which are very little to be envied, will probably only be able to dispose of their supplies at considerable sacrifice. In any case, we do not believe that it will be possible to keep up the prices until the principal quantity of this year's oil has been disposed of, when there would be real justification for a greater firmness in the market.

Crop results of the last 10 years.

1909	4319 kilos	1904	5000 kilos
1908	2652 „	1903	6250 „
1907	2513 „	1902	3200 „
1906	4625 „	1901	3050 „
1905	4150 „	1900	4250 „

Parry[1]), having examined four authentic samples of rose oil of the present years's crop has found them to possess the following properties: $d_{30°}$ 0,8568 to 0,8573, α_D — 2°30′ to —3°, $n_{D25°}$ 1,4626 to 1,4630, after washing with water 1,4630 to 1,4638; m. p. 22,5°. Total geraniol content 68,5 to 71 %.

According to Parry's observations[2]), the adulteration of rose oil has continued to be practised on a large scale this year. Fewer

[1]) Chemist and Druggist **75** (1909), 186.
[2]) Ibidem 292.

Production of pure Rose Oil, tabulated according to districts.
Crop 1909.

District	kg.	g.
District of Kazanlik.		
Kazanlik	83	
Alexandrovo	162	
Achiklii	25	
Bahaslii	3	
Bitcherlii	10	
Borisovo	20	
Gabarevo	54	
Golemo-Selo	175	
Gussovo	11	
Gornïo-Sahrane	25	
Urenlii	25	
Dimovtzi, Brestva, Gergovetz, Tcherveni-Popové, Urta	22	
Doïmouchlaré	20	
Dolnïo-Soffoulare	10	
Elchovo	72	
Enina	122	
Saltakovo	10	
Karagitlii	31	
Kozloudja	45	
Kazalajderé	29	
Kachlata	21	
Lahanlii	36	
Dolnïo-Sahrane	21	
Maglige	105	
Nova-Machla	4	
Ovochnik	21	
Orosovo	42	
Pavel-Banïa	82	
Ragina	30	
Sekeretchovo	15	
Seltzi	6	
Simitleri	31	
Skobelevo	46	
Slivito	6	
Popovtzi	5	
Toulovo	12	
Touria	82	
Tarnitchane	32	
Hassat	15	
Himitlii	31	
Tchanaktchii	21	
Forward:	1618	

District	kg.	g.
Brought fwd.:	1618	
Tcharganovo	16	
Cheïnovo	26	
Chipka	84	
Aïkanlii	36	
Total:	1780	
District of Karlovo.		
Karlovo	124	
Adjar	60	
Arapovo	26	
Banïa	15	
Kalougerovo	2	
Begovo	6	
Bogas	32	
Voïnagovo	42	
Guilleré	37	
Gornïo-Kusseleré	77	
Gornio-Omarobas	30	
Kofalare	7	
Davadjovo	25	
Derelie	92	
Dolnïo-Omarobas	68	
Dougandjii	7	
Mintichlii	6	
Dabeni	39	
Aïganovo	24	
Ahievo	15	
Kara-Sarlii	36	
Kalofer	69	
Klissoura	48	
Kotchmalaré	25	
Karnare	17	
Achiklaré	29	
Madjaré	27	
Mitirisovo	41	
Michiltzi	29	
Mratchinik	16	
Ortchilaré	36	
Rahmanlaré	158	
Sindjirlii	19	
Slatina	47	
Sopot	22	
Tekia	26	
Himitlii	15	
Forward:	1394	

District	kg.	g.
Brought fwd.:	1394	
Hissar	8	
Hissar-Kusseleré	35	
Tchoukourlii	24	
Kourtovo	11	
Total	1472	
District of Plovdiv.		
Babek	18	
Brezovo	14	
Demirdjileri	11	
Doudeni	13	
Panitcheri	28	
Aïreni	14	
Rachmanlii	160	
Seldjikovo	5	
Staro-Novo-Selo	70	
Oustina	19	
Total	352	
District of Nova-Zagora.		
Balabanlii	14	
Bosagatch	2	
Djoumalii	2	
Zapalnïa	16	
Kispetlii	6	500
Kriva-Kroucha	5	
Smavli	3	
Nicolaevo	11	
Orisari	—	500
Tvarditza	46	
Tersiobass	—	500
Dolnïo-Tchanaktchii	18	
Kososmadé	26	
Hainito	18	
Konaré	24	
Total	192	500
District of Stara-Zagora.		
Stara-Zagora	6	
Ada-Tepé	8	
Arnaoutito	9	500
Beltchevo	3	
Djambazito	—	500
Dalboki	14	
Zmeevo	6	
Kazanka	23	
Kolena	14	
Nova-Machla	6	
Orechovitza	16	
Forward:	106	

District	kg.	g.
Brought fwd.:	106	
Haïdanlii-Mouratlii	3	
Hamzalari	9	
Koutloudja	8	
Hrichteni	17	
Echerkovo	12	
Total	155	
District of Tchirpan.		
Tchirpan	—	
Alagun	28	
Baldjilaré	9	
Golemo-Derelie	8	
Enicher	12	
Echevren	3	
Kalfa	5	
Kolatchevo	19	
Konoptchii	4	
Nova-Machla	5	
Sadaklii	22	
Sakarlii	7	
Tchehlaré	40	
Assakarovo	23	
Mahmoutlare	8	
Hadjiollare	8	
Total	201	
District of Pechtera.		
Pechtera	4	
Bratzigovo	69	
Bega	5	
Kozarsko	27	
Kritchim	6	
Tchanaktchievo	11	
Total	122	
District of Pazardjik	16	
„ „ Panagurichte	24	
„ „ Stanimaka	5	
Total	45	
Recapitulation.		
District of Kazanlik	1780	
„ „ Karlovo	1472	
„ „ Plovdiv	352	
„ „ Nova-Zagora	192	500
„ „ Stara-Zagora	155	
„ „ Tchirpan	201	
„ „ Pechtera	122	
„ „ Pazardjik	16	
„ „ Panagurichte	24	
„ „ Stanimaka	5	
Total	4319	500

Exports of Rose Oil 1908 and 1909.

Countries	From 1st January to 31st Dec. 1908	From 1st January to 31st March 1909
	kilos	kilos
Austria-Hungary	48	7
Belgium	4	—
France	1422	106
Germany	760	225
Greece	0,125	0,125
Italy	44	6
Netherlands	2	2
Other countries	—	0,250
Roumania	0,250	0,250
Russia	183	28
Servia	0,400	—
Sweden	2	—
Switzerland	56	10
Turkey	77	11
U. K.	1141	251
U. S. A.	872	138
Total	4611,775	784,625

instances of the addition of alcohol have been observed, but many cases of adding geraniol and similar bodies which alter the physical constants only very slightly, but which betray themselves by the increase in the geraniol content. Five such sophisticated samples, which had been sold as "guaranteed pure oil", contained from 79,5 and 82 % of total alcohol, whereas pure rose oils contain not over 75 %. Hence Parry, in common with ourselves[1]), regards the determination of the total geraniol content as a most important factor in judging the value of a rose oil.

We ourselves recently handled a Bulgarian rose oil which was sophisticated with both adulterants at the same time. The original sample only behaved a little abnormally as regards the index of refraction, but the indications of adulteration were apparent as soon as the oil had been extracted with water. The sp. gr. at 30° was thereby increased from 0,8606 to 0,8632, the index of refraction from 1,46565 to 1,46674 and the congealing point from + 20° to + 21°. We were able, by fractional distillation, to isolate from the water of extraction about 10 % of alcohol (calculated for 90 per cent. alcohol). The sp. gr. which was suspiciously high for rose oil, and the index of refraction, which was much too high, in conjunction with the abnormal geraniol-content which, even after removal of the alcohol, kept at 78,5 %, point to the conclusion that palmarosa oil as well as alcohol had been added.

[1]) Comp. Report November 1908, 104.

Rose Oil, German. This year's harvest in our fields at Miltitz has been carried out under normal conditions, although, owing to the coolness of the weather, with some delay. Bright, but not too warm weather during the flowering time allowed the roses to unfold gradually, so that we were able to avoid a sudden accumulation of gathered flowers. Notwithstanding this, the oil output has left something to be desired, although it has not been necessary on this account to raise the prices. As regards quality, our rose oil of this year's crop is quite worthy of its predecessors.

Rosemary Oil. For Dalmatian rosemary oil the same price is asked as last year, but it appears to us probable that within the next few months the market may be expected to give way. Since rosemary oil has ceased to be used for spirit denaturing to the same extent as formerly it will become more difficult to find an outlet for the production, which has not grown less. French rosemary oil has shown a rising tendency and the market continues firm, notwithstanding the competition of the Tunisian oil, which, although not quite equal to the French oil in quality, is frequently offered at lower rates. Detailed reports about the article are wanting, but we shall probably be justified in assuming that, as in the case of spike oil, the distilling season this year is likely to give only a moderate result.

Samphire Oil (*Essence de criste-marine*). From samphire (*Crithmum maritimum* L., N. O. Umbelliferæ), an oil may be obtained which, up to the present, has been but little investigated, the only known references concerning it in literature occurring in some old investigations by G. Lavini and H. Herouard[1]). According to a recent publication by F. Borde[2]) an essential oil has been distilled from the plant gathered almost at the end of the flowering season. The plant contained 80% of water. The oil-yield was as follows. Of plants collected in the first half of August, leaves and stems gave 0,3%, fruit 0,7%; in the second half of August 0,15 and 0,8%, and in the middle of September 0,154 and 0,7% respectively. The oil from the leaves and stalks is specifically heavier than that from the fruit; it has a deep-yellow colour, and an aromatic, somewhat pungent odour of the plant. The crushed fruits, however, yield a pale yellow oil, which has a pleasant odour, especially when the fruit has een air-dried. The subjoined table gives the properties of the oil from the various parts of the plant, "A" being oil from leaves and stems, "B" from fruit.

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[1]) Mem. della Reale Acc. delle Scienze di Torino **25**, 13; Journ. de Pharm. et Chim. IV. **3** (1866), 324.

[2]) Bull. des Sciences Pharmacol. **16** (1909), 132. Through Chem. Zentralbl. **1909**, I. 1566.

	August		about mid-September	total samples		dried fruit
	1st half	2nd half				
d_{40} (A) . . .	1,0374	1,0519	1,0492	—	—	—
„ (B) . . .	0,9690	0,9730	0,9661	0,9809	0,9808	0,9581
α_D (A)[1]) . .	8° 15′	7° 12′	6° 42′	—	—	—
„ (B)[1]) . . .	5° 27′	6° 4′	6° 12′	5° 32′	6° 4′	8° 9′
Iodine no. (A)	189	167	153	—	—	—
„ „ (B)	215	201	210	192	199	174
Sap. no. (A) .	6,4	—	—	—	—	—
„ „ (B) .	10	—	—	—	4,2	—
Acet. no. (A)	1,2	—	—	—	—	—
„ „ (B)	—	—	—	—	3,5	—

In addition to the above data, the b. p. (170 to 300°) and the solubility in alcohol (1 : 6 of 90 per cent. alcohol) of the oil distilled from ripe and dried fruit are recorded.

In the fractions boiling over 200°, which M. Delépine[2]) examined more closely, he proved the presence of dill apiol, possessing the following constants: b. p. 294 to 295° (corr.) with slight decomposition, 157 to 158° (corr., at 13 mm.), $d_{4°}^{13°}$ 1,1644, $n_{D25°}$ 1,52778. Mol. refr. found 59,20; calc. 58,28. For closer identification, Delépine prepared the tribromo-compound, $C_{12}H_{13}BrO_4Br_2$, m. p. 110°, and he also converted the dill apiol into dill *iso*apiol, m. p. 44°, by treating it with sodium ethylate. From the latter combination the author, by oxidising with iodine and mercuric oxide, obtained dimethoxy-2,3-methylene-dioxy-4,5-hydratropa aldehyde, $C_9H_9O_4 \cdot CH(CH_3)CHO$, a liquid boiling at 189° (17 mm.) and possessing the following properties, viz., $d_{4°}^{17°}$ 1,2407, $n_{D25°}$ 1,53191; mol.-refr. found 59,79, calc. 58,96; m. p. of the oxime 102°, of the semicarbazone 148°. Oxidation with oxide of silver yielded the corresponding acid $C_9H_9O_4 \cdot CH(CH_3) \cdot CO_2H$, m. p. 119.

As the oil contains about 40 to 60% of dill apiol, *Crithmum maritimum* offers a cheap and rich raw material for the preparation of dill apiol[3]) which was hitherto difficult to obtain.

Sandalwood Oil, East Indian. Business in this article has been so extraordinarily brisk that in spite of the considerable enlargement of our distilling plant we have at times hardly been able to cope with the demand.

The following table, showing the quantities of sandalwood sold in last year's auctions and by tender in the State of Mysore, also the

[1]) Direction not stated.
[2]) Compt. rend. **149** (1909) 215.
[3]) Report April **1903**, 30; November **1908**, 50.

amount realised therefrom and the accompanying comment supplied by the Government will interest our readers: —

No.	District	Khoti	Auction sales		Sales by tender		Total sales	
			Quantity	Amount	Quantity	Amount	Quantity	Amount
			ts. cwts. lbs.	Rs. a. p.	ts. cwts. lbs.	Rs. a. p.	ts. cwts. lbs.	Rs. a. p.
1	Mysore	Hunsur .	403 10 0	210023 1 7	96 10 0	51030 0 0	500 0 0	261053 1 7
2	Mysore	Seringapatam .	140 3 84	73920 5 5	85 15 0	43424 12 0	225 18 84	117345 1 5
3	Bangalore	Bangalore . .	66 9 98	32259 7 8	26 3 86	15246 11 9	92 13 72	47506 3 5
4	Hassan	Hassan .	70 8 14	36425 4 6	73 1 0	36302 4 0	143 9 14	72727 8 6
5	Kadur	Chikmagalur .	254 17 0	121450 9 7	83 14 0	46190 0 0	338 11 0	167640 9 7
6	Kadur	Tarikere	181 4 35	95609 4 1	28 15 84	14962 2 0	210 0 7	110571 6 1
7	Shimoga	Shimoga	160 7 0	47681 3 2	171 5 0	100718 12 0	331 12 0	148399 15 2
8	Shimoga	Sagar . .	56 12 56	27837 11 9	9 0 0	945 0 0	65 12 56	28782 11 9
9	Shimoga	Tirthahalli . .	178 5 0	84097 15 8	—	—	178 5 0	84097 15 8
		Total	1511 17 63	729304 15 5	574 4 58	308819 9 9	2086 2 9	1038124 9 2

Of the total quantity of 2487 tons 14 cwts. 72 lbs. exposed for sale, 2086 tons 2 cwts. 9 lbs. were disposed of both by auction and tender for Rs. 1038124.9.2 against 2482 tons 14 cwts. 47 lbs. disposed of in the previous year for Rs. 1365577.2.5.

The quantity exposed for sale was less than that of the previous year by 56 tons 13 cwts. 57 lbs.; and the quantity sold was less by 396 tons 12 cwts. 38 lbs. The realisation was less by Rs. 327462.9.3. The quantity left unsold is 401 tons 12 cwts. 63 lbs. The reason for this unsatisfactory result, so far as can be gathered from enquiries and published reports, seems to be limited demand in America and Europe for essential oils owing to the financial crisis and consequent depression of trade. It is stated that the principal continental distillers have held large stocks and did not indent for their usual annual supplies. The causes are therefore temporary and will cease as soon as the normal prosperity is restored. The China market is now absolutely closed to India, as it is now being supplied with an inferior kind of cheap wood from Australia. The Chinese, it is said, use sandalwood only for ceremonial purposes, such as cremation and burning in temples and not for distillation as in Europe and India, hence it is a matter of little consequence to them what kind of wood they use. However, samples of the various classes of Indian wood have been sent to merchants there with a view to ascertain whether there is likely to be any market for them; but it seems there is little probability of China again becoming a large buyer of Mysore wood.

The undermentioned details concerning the forthcoming auctions have so far come to hand: —

No.	District	Khoti	Date of sale	Approximate quantity
1	Shimoga . . .	Tirthahalli	18th Nov. 1909	200 tons
2	„ . . .	Sagar	22nd „ 1909	100 „
3	„ . . .	Shimoga	25th „ 1909	500 „
4	Kadur . . .	Tarikere	29th „ 1909	200 „
5	„ . . .	Chikmagalur	2nd Dec. 1909	400 „
6	Hassan . . .	Hassan	6th „ 1909	200 „
7	Bangalore . .	Bangalore	9th „ 1909	100 „
8	Mysore . . .	Seringapatam	13th „ 1909	250 „
9	„ . . .	Hunsur	16th „ 1909	450 „
			Total	2400 tons

Sassafras Oil. Short notes on a new use for sassafras oil have been published[1]). It is reported that this oil has been successfully employed for the destruction of the eggs of lice, and also against the bites and stings of insects. If applied immediately after the sting, the oil is said to prevent all disagreeable after-effects. A camphor oil containing safrol has been employed for similar objects.

As is well known, eugenol, which chemically is closely allied to safrol, is used for similar purposes.

Savin Oil. In criminal cases it may be, in certain circumstances, a matter of the greatest importance to be able to prove the presence of small quantities of oil of savin. Beythien and Atenstädt[2]) have searched through technical literature for data showing how this can be done, but all they have discovered is a few colour-reactions described by Jaworowski, and these, as was to be expected, gave no typical identifications. Beythien and Atenstädt declare that this also applies to the furfurol and bichloride of tin tests, which they applied for the detection of oils of savin and juniper-berries. These tests, like all colour-reactions, require a certain skill in their application and leave the operator entirely in the lurch when less than 10% of savin oil is present. The authors are of opinion that the determination of constants only can supply sufficient data for certain detection, but it is probable that in only very few cases sufficient material would be available for the determination of constants, and that the only factor which it would be possible to determine would be the optical rotation. For this purpose (assuming the abstract from which we quote to represent correctly the authors' proceedings), it is said that one single drop will suffice, but we are unfortunately without particulars of the manner in which this determination is to be carried out.

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[1]) Pharmaceutical Journal **82** (1909), 665, 729, 787.

[2]) Zeitschr. Untersuch. der Nahrungs- u. Genußmittel **16** (1908), 677. Through Pharm. Zentralh. **50** (1909), 345.

Schinus Oil. Roure-Bertrand Fils, in their last April report[1]), give detailed particulars of *Schinus molle* L., and of the oils obtained from it. The tree, which is also known, from its native place and its fruit, as "American pepper", belongs to the Terebinthaceæ, a subfamily of the Anacardiaceæ. Of the oils described in the report, two came from Algeria, one of these being distilled from leaves only, the other from the branches, with the leaves and fruit. A third oil, of French origin, was distilled at Grasse from entire branches. The table below gives the constants of these oils, together with those previously obtained by us[2]) from Mexican oils. The difference lies chiefly in the greater lightness and the more sparing solubility of the Mexican as compared with the Mediterranean oils. The optical rotation differs according to the source of origin, but, singularly enough, the divergencies between the properties of the oils obtained from the different parts of the plant are less pronounced. The oil-yield from the berries only, however, was larger than that from the brenches and leaves.

	Algerian oils		French oils from Grasse	Mexican oils		
	entire branches	leaves	entire branches	leaves	fruit	undetermined
$d_{15°}$	0,8634	0,8658	0,8696	0,8583	0,8600	0,8492
α_D	+50°54′	+65°20′	+46°13′	+44°50′	+42°30′	+56°27′
$n_{D20°}$				1,47665	1,47909	1,47616
acid no.	—	0,7	2,1			
ester no.	5,5	3,4	8,2	7,2	25,2	
ester no. after acet.	29,4	40,4	43,4		56,5	
solub. in 90 per cent. alcohol	5 vol.	5 vol.	10 vol. with turbidity	Even with absolute alcohol the solution, at first clear, becomes turbid when more alcohol is added.		

Oil of Sium cicutæfolium. From the green herb of *Sium cicutæfolium* Gmel. (Umbelliferæ), a native of South Dakota, F. Rabak[3]) obtained 0,5 % of essential oil, of a pale yellow colour and a pronounced odour of caraway, at the same time reminding of turpentine. The oil gave a cloudy solution with 6 parts of 90 per cent. alcohol; $d_{22°}$ 0,8447; α_D + 63° 40′; acid no. 0; ester no. 33, corresponding to 11,55 % of ester $C_{10}H_{17}OCOCH_3$. Compared with the original oil, the acetylated sample showed no increase in the ester number; free alcohols are therefore not present. Its pronounced rotation to the right indicated the presence of d-limonene. A reaction for aldehydes was obtained both with magenta solution and with nitrate of silver.

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[1]) Berichte of Roure-Bertrand Fils, April **1909**, 36.
[2]) Report April **1908**, 121; April **1909**, 83.
[3]) The Midland Drugg. and Pharm. Review **43** (1909), 5.

Spearmint Oil. According to the reports from our informant, an abundant crop may this year be expected in the United States, as both in Michigan and in Indiana extensive new plantations have been laid down. The demand for this oil by the American manufacturers of chewing gum has fallen off considerably, and it is hoped that low prices will prevail in the autumn. We invite firms who desire to treat for large parcels of late delivery to solicit quotations, as through our New York branch we are in an excellent position for supplying the article to advantage.

Spike Oil. The distillation has been a little in arrear this season, and for the present it is impossible to make any announcement as regards the prices of the oil. According to preliminary reports only a moderate output is to be expected in the departments of the Basses-Alpes, Vaucluse, Var, Bouches-du-Rhône, and Drôme. The information from the Gard and the Hérault is still more indefinite.

As stated fully in our last November Report[1]) we discovered in the course of the year 1908 that really good spike oils dissolve in 5 to 15 vols. of 60 per cent. alcohol, and that a markedly inferior degree of solubility may probably invariably be due to adulteration. We therefore suggested that it be made a condition that spike oil should give a clear solution with 15 to 20 vols. of 60 per cent. alcohol and at the same time we stated that it would be our endeavour henceforth to supply only oils which stood this test. Unfortunately the wish which we then expressed that we might always be able to observe these conditions has not been fully realised. In spite of the most painstaking efforts we have not succeeded in covering our requirements of superior, readily soluble spike oil altogether at normal prices, and we have therefore decided henceforth to list two varieties of spike oil, namely an easily soluble quality (1 : 15 to 20 vols. 60 per cent. alcohol), and the present variety, soluble in 70 per cent. alcohol (1 : 1,5 to 3 vols.).

Star anise Oil. There is not much to be reported concerning this article. In the course of the summer some important transactions were put through at 4/-, after which the quotations again advanced by about 2 d., and at this level they appear to be inclined to stay, notwithstanding the dull tendency of the Chinese silver-market. Hence it may be surmised that no heavy stocks remain in China.

Tansy Oil. The price of this article, which is a speciality of our New York branch, has fortunately been somewhat reduced in the course of the last few months, and when this year's distillate from

[1]) Report November **1908**, 115.

the cultivations in Michigan and Indiana, which have now been extended to about 150 acres, is available, the value may go down still more. An output of about 1500 lbs. is expected, which, in view of the rather restricted consumption, may be regarded as sufficient.

Turpentine Oil. According to official reports[1]) the total quantity of oil of turpentine produced in the United States between April of last year and March of the present year amounted to over $36^1/_2$ million gallons, and that of rosin to over 4 million barrels (each averaging 280 lbs. gross). The values were $ 14112000 and $ 17784000 respectively. As compared with the preceding year, the quantity of oil of turpentine was 2,4 million gallons and that of rosin nearly 290000 barrels larger. The value on the other hand was 4,17 million dollars less for the oil and 465000 dollars more for the rosin than in 1907. The highest price reached by the oil in the course of the year 1908 was 50 cents per gallon in April; from that period onwards the price fell to 35 cents in October; it then rose again to $41^1/_2$ cents, and at the end of the business year it closed at 37 cents. In the course of 18 months the decrease in value was about 50 %.

The increased production in the year 1908 is attributed less to the increase in the number of places of production (1696 in 1908, as compared with 1629 in the previous year) than to the more favourable conditions of weather and labour. The British Consular report explains the latter as being the result of the unfavourable condition of the lumber industry, brought about by the general economic crisis.

It is worthy of note that in 1908 for the first time the value of the rosin produced exceeded that of the oil of turpentine: —

Year	Oil of Turpentine	Rosin
1900	$ 14960335	$ 5129268
1905	„ 15170499	„ 8725619
1907	„ 18283309	„ 17317059
1908	„ 14112377	„ 17783509

In view of the threatened situation of the turpentine industry in the Southern United States, the Department of Forestry of the Republic, through its expert in the turpentine and rosin industry, Mr. George B. Sudworth, has published a report on what is called "Conservative Turpentining", which has been reproduced in its entirety by an

[1]) Report of the German Consulate in Atlanta and Report of the Commercial Expert of the German Consulate-General in New York. According to Nachrichten f. Handel u. Industrie No. 55, p. 4, May 25th 1909 and No. 70, p. 4, 1st July 1909. Diplomatic and Consulate Reports No. 4199, p. 10, April 1909.

American technical paper[1]). The object of this exhaustive article is to indicate means by which the turpentine industry may attain some measure of stability, not alone by the application of less destructive processes in the preparation of the crude resin by means of the so-called "cup and gutter system" (to which we have already referred on a previous occasion)[2]), but also by the adoption of recognised scientific methods of forestry in the extension of the turpentine industry to new forest areas, and especially by utilising the trees not only for the purpose of obtaining turpentine, but also for subsequent use as lumber.

The report considers in sequence the different varieties of pine tree used in the production of naval stores (oil of turpentine and colophony), the collection of the resin from the tree according to the old and destructive "box" method, and its further conversion into oil and rosin. With regard to these points we have made extensive references in earlier reports, and we may also refer to Gildemeister's and Hoffmann's *The Volatile Oils*, p. 239. On the subject of the area in which turpentine is produced, the report states that Virginia and the flat coast-districts of North and South Carolina are almost entirely exhausted, and are scarcely to be considered any longer as producing districts, the principal area of production having been removed further South, towards the mouth of the Mississippi. The principal States where the products are now obtained are Florida, Georgia, and Alabama. In Texas the owners of forests are averse from tapping the trees, as they fear that by doing so the value of the wood for subsequent use as timber migth be impaired. This is, in fact, the case when the resin is produced by the ruinous "box" system, but the fear is unfounded if the "cup and gutter" system is followed, and the last-named process moreover yields from 20 to 30% more oil of turpentine than the other, owing to the decreased evaporation of the gum which is collected, while at the same time it produces a paler coloured rosin. Under the present conditions — where $^7/_8$ of the trees are exploited by the old, and only $^1/_8$ by the new process —, it is calculated that the production of turpentine and rosin cannot last more than from 25 to 30 years. The advantages of the "cup and gutter" system, upon which the report lays particular stress, are made still more clear by a modification of that system which has been experimentally tried by the Forestry Department during the last 3 years with about 80000 trees. This consists in cutting streaks into the bark of the pine-trees, by means of a hack of special shape, of only from $^3/_8$" to $^1/_2$" depth and from $^1/_8$" to $^3/_{16}$"

[1]) Oil, Paint and Drug Reporter **75**, No. 11, p. 10, 15th March 1909.
[2]) Report April **1906**, 65.

height, as compared with incisions of from 1″ to 1½″ depth and ¼″ to ½″ height made by the process now in use. The further advantage of the modified system is said to consist in the fact that a given forest area, instead of being exhausted as at present in from 4 to 5 years, can be worked for turpentine for from 15 to 20 years and even for twice that length if it is desired to exhaust the trees to the uttermost before lumbering. Further, instead of from 19 to 20%, it is said that the resin will yield from 22 to 25% of oil, while the vitality of the trees is affected in the smallest possible degree, and is not destroyed. Further experiments to be made by the Forestry Department will clear up the point whether young trees not yet fully grown can also be turpentined by the new process without damage to their development.

In continuation of its efforts to introduce a less destructive treatment of the turpentine producing trees, the American Forestry Department, through its expert Mr. A. L. Brower, has published a treatise on the method of turpentine-preparation which prevails in France. This has also appeared in the periodical referred to above.[1]) The French process makes it possible to tap the same tree for 30 years or more without injurious consequences and without reducing the yeld of turpentine. By the old American "box" method, on the other hand, the tree yields resin for 5 or 6 years only, and by the new "cup-and-gutter" method, by which the trees are tapped lengthwise, from 15 to 20 years. It must be admitted that the French process does not yield so large a result as the American. It is also more laborious and requires workmanlike practice; and in view of the entirely different economic conditions of the two countries, it is extremely doubtful whether the American forest owners will ever adopt the French method.

The salient features of the French method consist in stripping the trees as far as necessary of their outer bark, and in not beginning to tap the trees until they are at least 15 years old. About the beginning of March a tapping-space is cut into the trees quite close to the ground by means of an axe of particular shape with a convex cutting edge placed at right angles to the axis of the shaft. This tapping surface is about ½″ deep and about 4 sq. in. in area. Below this spot a curved cutting is made with a chisel and in this a bent strip of tin, shaped like a trough, is placed for the purpose of receiving and conducting the resin. Below this, wedged in between the strip of tin and a nail driven into the tree, is the cup intended for collecting the resin. Between March and the middle of October the tapping place is enlarged about 30 times in an upward direction, each time from ½″ to 1″, the depth of the incision (½″)

[1]) Oil, Paint and Drug Reporter **75**, No. 18, p. 28, 3rd May 1909.

remaining the same; so that at the end of the collecting period the tapping area is about 26″ long. In the course of the 4 following periods of tapping the process is continued upwards in a similar manner so that at the end of about 5 summers the tapping area has reached a height of about 12 ft. At fixed distances throughout this height cups are placed which are emptied once a fortnight and cleaned, together with the strip of tin, the tapping area being also scratched off from time to time. After about 4 years, when the first tapping-surface has attained the height mentioned, a second cutting is begun at a distance from the first of about one-third of the circumference of the tree, and after 4 more years a third similar cutting is started. At the end of the last-named period the tree is tapped again by the introduction of fresh cutting surfaces in the neighourhood of the first, but only one cutting may then be made every year.

After 8 or more of these cuttings it is customary to fell the tree. This considerate treatment (*gemmage à vie)* gives an annual yield of from 3 to 5 lbs. of resin for every cutting area; while the exhausting mode of tapping *(gemmage à mort)* in which several tapping areas are made close together and are worked for 3 years only (after which the tree is cut down) yields from 18 to 20 lbs. a year.

The exports of resin and pitch from Bordeaux in 1908 amounted to 39708 tons, this being an excess over 1907 of 8209 tons; the exports to the United Kingdom amounted to 14247 tons, being an excess of 4404 tons[1]).

With regard to the turpentine industry in the Departments of the Charente, Gironde, Landes, and Lot-et-Garonne, it is stated to be almost entirely in the hands of a few large proprietors of forests, who also buy up the produce of the smaller owners. Recently, however, Companies have been formed with foreign capital which work according to patented methods and many proprietors and turpentine dealers have also formed Co-operative Societies. These societies, however, have hardly affected the fundamental character of the industry, which consists in division by communes, each working on its own account. The total number of the plants at work is estimated at 220, with an annual output of about 220000 barrels of pitch and colophony of about 7 arts each. The favourable condition of the turpentine industry in South-Western France is shown by the average prices of resin, oil, and rosin in the years 1906 until 1908.

The total exports from Bordeaux were as follows: —

	1906	1907	1908
Turpentine oil	8737 tons	5712 tons	3912 tons
Resin, pitch etc.	28177 „	31499 „	39708 „

[1]) Diplomatic and Consular Reports Nr. 4246, p. 16, 24, 35, June 1909.

of which the exports to the United Kingdom amounted to: —

	1906	1907	1908
Turpentine oil	1 400 tons	1 524 tons	1 169 tons
Resin, pitch etc.	8 356 „	9 793 „	14 197 „

The turpentine oil works of the Indian Government at Dehra Dun, to which we have previously referred [1]) are, as we learn from a technical paper [2]) about to close down. The plant at Nurpur, which has only been at work for 6 years, has also been laid idle. The only turpentine oil distillery in India which is working satisfactorily (the name is not stated) has recently doubled its capacity. As pointed out by us on a previous occasion, the plant at Dehra Dun, which commenced work in 1888, was from the beginning placed in a rather difficult position owing to its great distance from the turpentine forests, and its closing therefore does not come as a surprise.

An American Consular Report gives details with regard to the situation of the Russian turpentine industry [3]). As is well known, Russian oil of turpentine is chiefly produced, not from the turpentine balsam by steam distillation, but as a bye-product when distilling wood. The industry is centred in the Northern, Eastern and Western Governments of Russia and in the Governments of the Vistula. In the district of Shenkur almost 75 % of the population are engaged in the production of oil of turpentine and pitch. The export value of the principal articles has been greatly reduced in the past year, as is shown by the following table: —

	1907	1908
Oil of turpentine .	1 949 000 Rbl.	1 292 000 Rbl.
Rosin	743 000 „	438 000 „
Tar	634 000 „	440 000 „

The reason why, in spite of the abundant material, the yield of oil and of pale rosin is small, is ascribed to imperfect technical practice. The best products are obtained in the Western Provinces, where the large output finds a ready sale abroad. A matter of interest is the increase in the exports of turpentine oil to Great Britain, as indicated by the following figures, which are taken from the British Import statistics: —

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[1]) Reports April **1905**, 78; October **1905**, 68; April **1906**, 64; April **1907**, 97; April **1908**, 102.

[2]) Chem. Ztg. **33** (1909) 808.

[3]) Oil, Paint and Drug Reporter **75**, No. 16, p. 51, 19th April 1909.

Imports from	1903		1905		1907	
	Quantity (cwts.)	Value ($)	Quantity (cwts.)	Value ($)	Quantity (cwts.)	Value ($)
Russia	56304	292744	68754	326624	93219	521453
France	14816	135147	28154	275059	19771	212169
United States . .	460324	4556672	424892	4733610	389828	3963920
Other countries .	1650	13597	4879	4879	7490	47104
	533094	4998160	526679	5374077	510308	4744646

According to the *Chemiker Ztg.*[1]), there are to be found in San Domingo pine forests which are extraordinarily rich in turpentine, and a local company is already engaged in manufacturing this product. A certain variety of pine, known as *Suaba,* is said to be so rich in rosin that the branches are used as torches.

We have on various occasions reported on methods for obtaining oil of turpentine from pitchy wood[2]). A new process of this kind, which is being employed in British Columbia for the utilisation of wood as well as of saw mill refuse, employs electricity — by which probably is meant the electric furnace.

According to an American Consular Report[3]), a demonstration was given at which two cords of wood were worked successfully for "turpentine oil", tar, oil, resin, pitch, and charcoal. The theoretical result promises the following rich yield: — per cord of resiniferous wood at $ 5, yielding chemically pure "turpentine oil" as well as the by-products mentioned above, of a total value of $ 24.70, the cost of production amounts to $ 12. The profit therefore should be $ 12.70, which appears to be confirmed by a number of experts familiar with the process and the production. It is stated that the yield per cord of wood is as follows: —

Rosin	60 lbs.
Tar oil	20 gallons
Charcoal	1300 lbs.

With regard to the last-named products, their usefulness as a wood preservative and in the manufacture of gunpowder is specially referred to. It is alleged that large quantities of suitable wood are available at low prices, and it is also stated that the plant has recently been increased to a capacity of 40 cords.

Apart from the question in how far a product of this kind, which should merely be termed pine tar oil, can be considered a sub-

[1]) Chem. Ztg. **33** (1909), 659.

[2]) Report April **1905**, 79; October **1905**, 67; April **1907**, 100; October **1907**, 93, 95.

[3]) Oil, Paint and Drug Reporter **75**, No. 20, p. 10, 17th May 1909.

stitute for pure oil of turpentine, it appears to us that the calculation has been made on a very liberal scale. No data are given as to the chief point, viz., the yield of "turpentine oil"; and it would also be of interest to be informed how, by the process described, the rosin is produced.

The first part of the latest Scientific and Industrial Reports of the firm of Roure-Bertrand Fils contains, *inter alia*, a paper by M. Vèzes[1]) on the turpentine industry in the French *Landes* and its products. Some years ago M. Vèzes, with the assistance of certain interested public bodies and private firms, established at Bordeaux University a laboratory devoted exclusively to the study of questions pertaining to the turpentine industry of South-Western France. In his present paper he gives an account of the mode of collecting turpentine in this region, accompanied by a number of illustrations. The account shows how carefully the French forest-owners husband their trees, in contradistinction to the wastefulness of the American turpentine farmers. As pointed out in the preceding pages, the American Forest Department is now taking steps to induce the owners of pine trees in the United States to adopt the French system of tapping. Vèzes further passes in review the work done in his laboratory, which up to the present was chiefly devoted to physics.[2]) The latest researches of which he gives particulars relate to the highest admissible degree of "normal impurities" in French oil of turpentine; by which he understands the slightly volatile substances, and colophony, as well as the degree of acidity. Small quantities of rosin pass over into the distillate either mechanically or because they are of low volatility; if the work of distilling is carried out in a slovenly manner it is self-evident that larger proportions of rosin may be carried over. Following previous proposals by Vèzes, the Commercial Union of the Resin-Industry at Bordeaux had fixed as the admissible maximum for turpentine oil 2,5 % of normal impurities and a degree of acidity not exceeding 1,0; the latter figure denoting the number of grammes of pure potassium hydrate which suffices to neutralise 1 litre of the oil (using phenol-phthalein as indicator). (Perhaps it would have been preferable, both for the sake of uniformity and in view of the variable sp. gr. of the oils, if the acid number had been fixed per kilo of oil, because in that case the acidity would have been identical with the general acid number in essential oil investigations.) For oils which, although free from "abnormal impurities" (benzene and petroleum distillates) yet indicate higher proportions of rosin and acids, the following classification has been laid down: 1. A normal oil of fair market

[1]) Berichte of Roure-Bertrand Fils, April **1909**, 3.
[2]) See Reports April **1904**, 86; April **1905**, 76; April **1907**, 99.

quality contains at most 2,5 % of "normal impurities" and not more acids than correspond to degree of acidity of 1,0. 2. Second class oil: maximum of impurities 3 %, ditto of acidity 3,0. 3. Third class oil: respectively 5 % and 5,0. 4. Oils which show figures exceeding 5 % and 5,0 respectively are to be regarded as adulterated.

Other researches by the same author, of which only a synopsis of results is given, had for their object the better separation of crude turpentine into two layers: water and pure turpentine; the boiling point determinations of various mixtures of water, turpentine oil, and colophony; the determination of the composition of an oil-and-water mixture passing over at definite temperatures, and, finally, controlling tests for these conditions in works-practice, the object of the whole being to prepare a heat-chart for turpentine distillation. After referring to his previous work on separation-curves of mixtures of water, alcohol and oil of turpentine, Vèzes reports on experiments in the preparation of rosin acids from colophony. To the latter, however, we will not refer in detail, as they are outside our sphere of interest.

While in most of the methods which have been proposed for the testing of oil of turpentine chemical processess are employed in order to ascertain the normal character of the oil, Geer[1]) proposes to estimate the purity of oil of turpentine by determining the principal physical constants of the oil after fractionating by water-distillation, with the assistance of a suitable distilling head, or of the fractions themselves. The reason why Geer uses water-distillation of the oil is to avoid superheating, which cannot be avoided in the case of dry distillation owing to the height of the condenser. This superheating would of course influence more or less the constants of the oil-fractions. The examination is carried on as follows: Exactly 500 g. of the sample are placed in a boiling flask. The still head, which is over one yard in height and in which 5 small funnels with horse-shoe shaped tubes have been placed in a suitable manner, is provided below the exit-tube with a thermometer divided into $^1/_{10}°$, as well as with a dripping-funnel from which during the process one drop of water per second runs into the still-head. A gentle steam-jet from a simple water-boiler provided with a safety tube and cock is introduced into the oil, so that two drops of the distillate pass over every second. The distillate is collected in separate fractions (usually 10 to 15), the size of which depends upon the rise in temperature, and therefore varies in different oils. The collection takes place in weighed measuring-glasses and by weighing the gross contents and deducting the weight of the water which

[1]) The analysis of Turpentine by fractional distillation with steam. U. S. Dept. Agriculture, Forest Service, Circular 152. Washington 1908. Chem. Ztg. **33** (1909), 859.

has also passed over, the net weight of the oil distilled over is ascertained. With every change of receiver the temperature is noted, in addition to which, apart from the odour and the colour, the weight as well as its percentage proportion to the total weight of the sample are determined and also its density and index of refraction. These four values, percentage proportion, boiling point, specific gravity and index of refraction, are placed in relation together by Geer and by the system of Cartesian co-ordinates he enters the figures representing the percentages by weight of the single fractions, as ordinates, the abscissæ are prepared once from the values for the boiling point, and next for the density and refraction. This graphic arrangement of the constants determined of each separate oil-fraction, gives a far better survey of the greater or smaller degree of uniformity of a sample than does the usual setting out of the values in tabular form, and makes it possible to compare at a glance the corresponding properties of different oils.

In this manner Geer has examined an oil of turpentine from gum, a crude "turpentine oil" obtained by steam distillation from wood, a refined oil of same origin, and lastly a crude oil obtained by dry distillation from pine wood.

It goes without saying that in all the oil samples before distillation the density and the refraction at 15° are ascertained, while colour, odour, etc., are also observed. Genuine oil of turpentine, under the co-ordinate system of percentage-figure and density, gave an almost perpendicular line, corresponding to the fact that up to 92 % distillate the density remained almost entirely constant; similarly the curve which was plotted from the relation between percentage and boiling point showed up to about 90 % of the height a course almost parallel to the axis of the ordinate. The curve which was plotted from the refraction showed, corresponding to the steady slight increase of the index, a direction gently inclining towards the axis of the ordinate, but this also shows at about 85 % a tendency to run parallel with the axis of the abscissa. The third oil sample consisting of purified oil obtained from wood by steam distillation also gave for the density a line running parallel to the axis of the ordinate, which only changed into a curve at 92 %. But for boiling temperature and refraction the lines which had run almost perpendicular up to 75 % height, changed into curves at that figure. From the almost equal course of the corresponding curves of the two oils, Geer pronounced the purified oil of turpentine from wood to be a very pure product of a quality equal to that of oil of turpentine from gum. The curves which were plotted from the constants of the fractions in the other two oils did not show the same regular course as those mentioned above; the curves of the oil prepared by dry distillation especially showed an entirely irregular

course, while those of the crude turpentine oil from wood distilled by steam more closely approached in their character the curves above described.

Geer considers the advantages of his method to lie in the use of the more considerate method of steam-distillation, of the principle of dephlegmation, in the application of the graphical method of expressing numerous data, which especially suitable for purposes of comparison, and finally in the application of a principle which has been followed with success in the practice of distillation on a large scale, and which according to his view can also be applied to the refining of oil of turpentine.

It would not be without interest to determine how, according to this method, which in reality does not contain anything that is new, but which places known properties into relation with one another, mixtures of pure turpentine oil from gum behave towards other "turpentine oils", and especially towards adulterants such as spirits of rosin, and fractions of mineral oils.

The complaints which are frequently heard in the United States as to increasing adulteration of oil of turpentine have induced the United States Department of Agriculture (according to an American periodical[1]) to invite a legal decision as to whether adulteration of oil of turpentine can be proceeded against under the Food & Drugs Act, in view of the fact that oil of turpentine is to some extent used medicinally. This intended proceeding by the Government is based upon the observation that for more than a year samples of oil of turpentine obtained from the stocks of the producers as well as of the first-hand buyers and wholesale and retail traders, were in fact found to be more or less adulterated when officially examined. The examination of the samples from the turpentine producing States gave the following results: —

	Producers' goods in yards primary buyers	Primary buyers' goods	Wholesale and retail dealers' goods
No. of samples drawn	64	40	76
No. of adulterated samples . . .	3	9	19
Percentage of adulterated samples .	5,0	22,0	25,0
Percentage of adulterant	2,9	1,6	5,6

Outside the turpentine producing States the condition of the samples was as follows: —

	Primary buyers' goods.	Wholesale and retail dealer's goods.
No. of samples . . .	5	115
No. of adulterations . .	—	31
Percentage of alterations	—	27
Percentage of adulterant	—	9

[1]) Oil, Paint & Drug Reporter **75**, No. 10, p. 9, 8th March 1909.

In commenting upon these figures the Secretary of State pointed out that the samples, with a few exceptions, were merely informal and that the quantities of the adulterant given must be regarded as minimum figures. The Secretary mentioned spirits of rosin and mineral oil as among the adulterants. On the ground of these results the Department intends to try to obtain a conviction under the Food & Drugs Act, which shall constitute a decision that may be used as a precedent. In the meantime, five such prosecutions have terminated with conviction.

E. H. Gane and M. H. Webster[1]) report on the ordinary substitutes for adulterants of oil of turpentine. Most nearly related to the pure oil (gum turpentine) are the so-called wood turpentines which are obtained by steam distillation from pitchy wood chopped small (steamed wood turpentine), or from the stumps of trees which have rotted or been cut down (stump turpentine), or again as a bye-product in the manufacture of wood pulp (wood pulp turpentine). Chemically these varieties of oils vary little, it is said, from genuine oil, and for technical purposes they are fully equal to it; but as a rule they have a more pungent odour. Recently, however, improved methods of purification have overcome this objection; in fact, oil distilled from wood often has a more pleasant odour than pure oil of turpentine. At the present time most of the oil of wood turpentine is obtained by dry distillation from resinous wood, and then purified by subsequent steam distillation. In this process pine tar oils of varying density are obtained as by-products, and these are used for the manufacture of turpentine substitutes. As regards suitability for the manufacture of paints and varnishes, it is said that wood turpentine possesses the same power of absorbing atmospheric oxygen, and therefore the same drying power, as gum turpentine.

Originally petroleum distillates were used as adulterants, both petroleum itself and petroleum benzine. Gane and Webster consider that the statement that spirits of rosin also is sometimes added is probably incorrect, because of the objectionable odour and dark colour of the latter. They themselves have not come across any oil adulterated in this manner. The oily character of petroleum and the high degree of inflammability of benzine led to the introduction as a substitute of the so-called "mineral base", which is obtained from heavy petroleum oils by the cracking process and subsequent careful fractionation of the product. It is possible that this distillate is useful as a solvent or diluent, but the properties of oil of turpentine can in no case be expected of it.

[1]) American Druggist and Pharmaceutical Record; through Pharmaceutical Journal 82 (1909), 684.

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In a note on the determination of petroleum in oil of turpentine, published as a supplement to a paper read before the Society of Public Analysts, J. H. Coste[1]) contradicts the statement of Turner that Armstrong's method of testing oil of turpentine (consisting of treating first with diluted and then with strong sulphuric acid)[2]) gives under certain circumstances values which are by 20% too low. Turner had made his experiments with a mixture of oil of turpentine and kerosene, but Coste points out that kerosene is a mixture of petroleum spirit, which is volatile under steam, and of non-volatile petroleum oil, whereas Armstrong's method especially applies to petroleum spirit — a fact overlooked by Turner. The latter's process of treating the upper layer of petroleum with strong sulphuric acid is more thorough than the method described above, and will probably only give accurate results when sources of possible error are mutually compensated. Experiments made according to Turner's method on mixtures of petroleum spirits and oil of turpentine, both of known physical properties and in different proportions, left an intact oil-mixture of higher refraction and density than those of the component parts; and it is surmised that terpinene and cymene were present as conversion-products of the terpenes. When the oil sample is freed from petroleum oil by steam distillation, and when for the rest Armstrong's original prescription is carefully followed, his process gives good results.

In the following discussion, Nash maintained that he was able to ascertain the quantity of petroleum spirits added by simply shaking known quantities of the adulterated oil of turpentine in a graduated tube with a definite quantity of air. According to his observations the height of the layer of froth which forms on an oil containing petroleum during the manipulation of shaking, stands in direct relation to the petroleum content. Pure oil of turpentine gives no froth. Of 14 tests recorded 9 agreed, the other 5 showed more or less pronounced deviations. Tatlock, who was in the Chair, asked whether other additions, such as spirits of rosin, could be determined by this method, to which Nash replied that he had not examined mixtures with spirits of rosin but only mixtures with petroleum spirits. Spirits of rosin, he thought, would hardly be used as an adulterant. Coste expressed his surprise at the agreement in the figures obtained by Nash. According to him the method proposed by Herzfeld[3]) of direct treatment with concentrated sulphuric acid, although based upon false premises, apparently gives approximately correct results. For accurate testing also Armstrong's process is very useful. Adulterations with petroleum are only very

[1]) Analyst **34** (1909), 148.

[2]) Gildemeister and Hoffmann, *The Volatile Oils*, p. 246.

[3]) Zeitschr. f. öff. Chem. **9** (1903), 454; Report April **1904**, 85; October **1906**, 78.

rarely observed in London, but more frequently in the North of England.

Vetiver Oil. Our unrivalled distillate from picked roots was in good demand, as usual, and we were able to supply sufficient quantities of it. The cheap Réunion variety has been offered plentifully, and when its producers complain of the low prices realised by the article, they must blame no one but themselves for this unsatisfactory state of things. In the first 7 months of 1909, 741 kilos were exported as compared with 275 kilos in the corresponding period of 1908. Over-production is here, as elsewhere, the order of the day.

As reported by Bacon[1]), vetiver or cuscus grass is also found in the Philippine Islands, where its roots are known to the natives as *moras* or *raiz moras*. A few sample distillations from root grown in experimental plantations gave the following result: Yield of the fresh crushed root: 1,09 % of a pale yellow oil. In order to separate the water better from the oil, which has almost the same specific gravity, petroleum was added, which was afterwards distilled off *in vacuo*. The oil possessed a strong, agreeable odour, and had the following constants; $d\frac{30°}{4°}$ 0,9935, $\alpha_{D30°}$ + 32,1°, $n_{D30°}$ 1,5212, sap. no. 47,4. Green root, not previously crushed, yielded upon distillation 0,3 % of oil, dried root, uncrushed, when extracted with ligroin, gave 0,25 % of oil with a very faint vetiver odour. Dried root which had been kept in sacks for 3 months, when distilled continuously by steam, with cohobation of the water, gave 0,456 % of a brown oil of powerful odour, possessing the following constants: $d\frac{30°}{4°}$ 0,9964, $\alpha_{D30°}$ + 32,1°, $n_{D30°}$ 1,5163, sap. no. 60,6. The experimental distillations were conducted with material varying in quantity from 65 to 175 lbs. The yield of root per acre is stated to be about 7200 lbs. The oil-content appears to increase up to the flowering time of the grass, and it would therefore probably be desirable to harvest and distil the roots when they are not more than three months old. The plants are propagated by dividing the roots; it has not been attempted to raise them from seed. According to Bacon the root can be distilled locally just as well as abroad, but in our opinion it would probably be more advantageous, from the point of view of the preparation of the oil, to ship the roots, because the rational distillation of the root is only possible with the resources of a large distilling establishment.

Bacon succeeded in detecting the presence of several acids in the oil. From 100 g. of the last-described oil he obtained by saponification 19 g. of an acid mixture whose odour reminded of fatty acid.

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[1]) Philippine Journ. of Sc. **4** (1909), A, 118.

After being twice distilled *in vacuo* this mixture yielded 40 % of a pale yellow, viscous acid, with an odour of oleic acid, which boiled at 200 to 205° at 4 mm. The analytical figures of the acid and its sodium salt gave the formula $C_{15}H_{24}O_2$. Genvresse and Langlois [1]) had discovered in vetiver oil an acid $C_{15}H_{24}O_4$ and they assigned the typical vetiver odour to the ester of this acid, containing the alcohol known as vetivenol $C_{15}H_{26}O$, which they also isolated. Bacon was unable to confirm this, because it was especially the neutral oils remaining behind after saponification which, according to his experiments, possessed a strong odour of vetiver. When these constituents were fractionated, the odour was found to adhere to the medium and higher fractions (b. p. 137 to 140°, and 140 to 145°, 12 to 15 mm.) and also to the semi-solid tarry residue, but not to the fraction with the lowest b. p. (125 to 133°). Another sample of vetiver oil yielded on saponification considerable quantities of benzoic acid.

Wild Cherry Bark Oil. As is well-known, the bark of the American Wild Cherry (*Prunus serotina* Ehrh., *Pr. virginiana* Mill., Rosaceæ), when stirred up with water, yields an essential oil consisting chiefly of prussic acid and benzaldehyde [2]). Although the constitution of the benzaldehyde points to the presence of a glucoside, attempts to isolate such a combination had not been successful. The fact that Hérissey [3]) obtained from a closely allied species, *Prunus Padus* L., mandelic-nitrile glucoside (amygdo-nitrile glucoside), made it probable that the same combination existed in *Prunus serotina*. F. B. Power and C. W. Moore [4]), have succeeded in proving that such is, in fact, the case. These investigators have published the results of an examination of the constituents of bark of *Prunus serotina* in which they state that in that portion of the alcoholic extract of the bark which is soluble in water, they have discovered the presence of l-amygdonitrile glucoside (m. p. 145 to 147° from acetic ester, $[\alpha]_D$ — 29,6°) although this body, it is true, only occurs in very small proportions. They also obtained tetraacetyl-l-amygdonitrile glucoside, which, recrystallised from alcohol, melted at 136 to 137°; $[\alpha]_D$ — 24,0° (in acetic ester). From the alcoholic extract they isolated by steam distillation, in addition to a small portion of benzoic acid, an essential oil, but in such a minute quantity that it was only possible to determine the b. p. (100 to 120° at 5 mm. press.). This oil had a pleasant aromatic odour, which was, however, altogether different from that of benzaldehyde.

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[1]) Compt. rend. **135** (1902), 1059; Report April **1903**, 76.

[2]) Bericht April **1890**, 48; Gildemeister and Hoffmann, *The Volatile Oils*, p. 444.

[3]) Journ. de Pharm. et Chim. VI. **26** (1907), 194; Arch. der Pharm. **245** (1907), 475, 641; Report April **1908**, 13.

[4]) Journ. chem. Soc. **95** (1909), 243.

The bark contained 0,075 % of hydrocyanic acid. A whole series of other, non-volatile, substances, was also found, but these are outside our purview.

Wintergreen Oil. There are no alterations to report in the price of this article. Plentiful supplies have been available and the tendency of the market is rather weaker. Only the Gaultheria variety („from the leaves"), which is much used in the United States, was scarce and dear.

Up to the present, cases of poisoning by methyl-salicylate, if any have occurred at all, have at any rate been very rare. Kobert[1]), for instance, reports that in spite of the very frequent use of the article, he has not been able to find anything on this subject in literature. A case of poisoning of this kind, however, has lately been made known in England through some periodicals[2]). This was a fatal case of poisoning caused by a very large quantity of methyl salicylate, which according to the public analyst probably amounted to possibly 300 to 400 grains. The existence of the ester was proved in the stomach, where most of it was found, and also in the urine, liver and kidneys. Dr. J. C. W. Graham, the medical officer, stated that he only knew of three similar cases in literature.

Wormwood Oil. The consumers are beginning to make the best of the fact that no considerable arrivals of French distillate are to be expected any longer and have lately again paid more attention to American oil, which for several years had been relegated to the background so far as commercial interest was concerned. From the reports received from our New York branch it appears that in America the increased demand has been met by extension of the cultivations, which are chiefly to be found in the States of Wisconsin, Michigan, Indiana, and New York. It is said that in Michigan and Indiana together there are 230 acres under wormwood, while the area cultivated in the State of New York is estimated at 14 acres. Up to the present the outlook is favourable, and it is therefore probable that as a result the prices will come out a little less than those now ruling.

As already previously announced, we are able to supply this year, for the first time, German wormwood oil of our own distillation, from material grown in our Miltitz plantations, where, in spite of the unfavourable weather conditions, the yield has been rather satisfactory. Our own oil is unrivalled as regards quality, and all who care for a really first class, aromatic oil will welcome it with satisfaction. We

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[1]) Kobert, *Lehrbuch der Intoxikationen*, 2nd Ed. 1906, II. 141.
[2]) Pharmaceutical Journal 82 (1909), 749; Chemist and Druggist 74 (1909), 816.

shall be glad to receive trial orders as soon as possible, as our stock is not likely to last very long. Next year we intend to enlarge our cultivations considerably.

In our last two Reports [1]) we mentioned that Rocques recommended Legal's test for the detection of wormwood oil in liqueurs. M. L. Cuniasse, who had already previously been investigating the same question has meanwhile written to us stating that he was the first who proposed this test for the same purpose, his suggestion having been published in 1907 [2]). We willingly take this opportunity of calling attention to the claim of priority made by M. Cuniasse.

For the purpose of judging the harmfulness of an absinthe liqueur, reference has been made, *inter alia*, to the degree of turbidity which ensues when absinthe is diluted with water. As already reported by us two years ago, Sanglé-Ferrière and Cuniasse [3]) have shown by experiments that the degree of turbidity affords no clue to the direct noxiousness of the liqueurs, but S. P. Krepieff [4]), in an inaugural dissertation, has again attempted to justify the diaphanometric method. His exposition is a little wanting in clearness, because the explanations given in his text do not always harmonise with the tables supplied by him. But it is fair to the author to add that his figures are only intended as a contribution to the problem, and that he expressly states that a final judgment can only be formed after new and more extensive experiments. We do not believe that the author's investig ations will be able to rehabilitate this rather insignificant method.

Ylang Ylang Oil. Business in this article continues to drag greatly, and although our "Sartorius" brand has continued to enjoy a normal demand, it is evident from the numerous offers that the output no longer stands in a proper relation to the requirements. The competition of the Réunion oil especially is assuming more and more serious proportions, for according to the official statistics to hand the shipments in the first half of 1909 reached not less than 1391 kilos, which was 476 kilos in excess of those of the corresponding period of 1908, but even more than the total of last year's exports.

We are informed that ylang ylang plantations have also been laid down lately on the island of Nossi Bé, which belongs to Mada-

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[1]) Report November **1908**, 127; April **1909**, 92.
[2]) Bull. Soc. Chim. IV. **1** (1907), 279. Also compare Report April **1907**, 94.
[3]) Journ. de Pharm. et Chim. VI. **25** (1907), 428; Report October **1907**, 98.
[4]) Essais diaphanoscopiques de la liqueur dite Absinthe et de ses imitations. Inaug. Diss., Geneva 1908.

gascar. It is said that the young trees number up to 25 000, and that they are flourishing so excellently that a considerable extension of the cultivation is already contemplated. According to preliminary estimates it is thought that the cost of production of the oil will be fcs. 100 per kilo (!). It will be seen that, if these statements should prove to be well founded, the overproduction is making further progress, to the certain ultimate commercial ruin of the article.

We have already discussed at some length in former Reports[1]) the cultivation of the plant yielding oil of ylang ylang; it will therefore suffice if we give a few facts from an article by L. Ozoux[2]) on the cultivation of ylang ylang on the island of Réunion by way of completion of what we have said previously. According to Ozoux, a good future harvest can only be expected when the trees are planted on a sheltered place and in good soil. A tree 10 years old and well-grown yields about 10 kilos of flowers annually. This is the average yield throughout the island; but there are some exceptional trees which produce as much as from 50 to 60 kilos of flowers yearly. Even taking only one-half of the annual crop, it may be estimated that the yield per year and per hectare (taking 400 trees per hectare) will amount to 2 000 kilos of ylang ylang flowers, from which 20 kilos oil of the first quality, or 40 kilos of the second quality (cananga oil) may be distilled. It is usual in Réunion to obtain second quality oil, because all the planters make the mistake of working only for quantity and not for quality.

Bacon[3]) confirms the classification of ylang ylang oil on the basis of its constants, which he published some time ago[4]). This confirmation rests upon the outcome of control tests made with 31 oils of the first, and 22 of the second, quality. The limits in the constants as now ascertained are as follows. First grade oils: $d_{4^\circ}^{30^\circ}$ 0,910 to 0,945 (mostly about 0,920 to 0,930), α_{D30° — 22 to — 50,8° (mostly — 40 to — 50°), n_{D30° 1,4863 to 1,4944, ester no. 92 to 129 (average 104), ester no. after acetylation 154 to 214 (average 182). Second grade oils: $d_{4^\circ}^{30^\circ}$ 0,905 to 0,925 (mostly about 0,910 to 0,915), α_{D30° — 38,5 to — 79,3° (fluctuating very irregularly), n_{D30° 1,4910 to 1,5030 (mostly keeping closely to the limit values) ester no. 71 to 88 (average 81), ester no. after acetylation 96 to 141 (average 118).

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[1]) Report April **1904**, 89; April **1908**, 120; November **1908**, 128; April **1909**, 94.
[2]) Journ. d'Agriculture tropicale **9** (1909), 131.
[3]) Philippine Journ. of Sc. **4** (1909), A, 127.
[4]) Philippine Journ. of Sc. **3** (1908), A, 65; Report November **1908**, 130.

Bacon has also instituted experiments for obtaining ylang ylang oil by extraction with the assistance of various volatile solvents, among which petroleum ether gave the best results. The yield was from 0,7 to 1,0% of an oil of very dark colour, containing fairly large proportions of resin. Undiluted, the oil had neither a particularly agreeable, nor even a powerful, odour, but when it was much diluted the perfume of the flower was clearly apparent. It had the following constants: $d\frac{30°}{4°}$ 0,940, $n_{D30°}$ 1,4920, ester no. 135, ditto after acetylation 208. It will be seen that these properties agree with those of first-grade distilled oils, and the slight difference in the odour of extracted oil as compared with the natural article is ascribed to the presence of small proportions of unknown compounds which are readily decomposed by heat. The extracted oil is also said to have this advantage that it cannot be imitated synthetically, and it is therefore possible that it may command much higher prices than distilled oil. When the extracted oil was shaken with water not inconsiderable quantities of resin separated out, which possessed the characteristic flower odour, while the residual oil assumed an odour of p-cresol methyl ether.

Zedoary Root Oil. According to statements by Bacon[1]) the parent plant of this oil, *Curcuma zedoaria* Rosc., grows abundantly in the neighbourhood of Manila. 100 kilos of the root of this shrub yielded 65 g. (0,065%) of oil, as well as 40 g. of a well crystallising volatile solid body. The oil was deep bluish-green and possessed an agreeable odour faintly reminding of camphor. $d\frac{30°}{4°}$ 0,933; $n_{D30°}$ 1,4920; probably inactive; in any case $\alpha_{D30°}$ not exceeding $+$ 1,5°; owing to the dark colour an exact reading was impossible. It dissolved readily in 2 vols. and more of 80 per cent. alcohol. When the parts with the lowest b. p. were distilled *in vacuo* the camphor-like odour, which is probably due to the presence of cineol, was lost, and its place taken by a true flower-odour. A more thorough examination of the oil is to be made later on.

The properties of this distillate agree closely with those which, up to the present, have been found with zedoary root oil[2]). The cineol-content of the oil was proved with certainty many years ago by ourselves[3]).

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[1]) Philippine Journ. of Sc. **4** (1909), A, 132.
[2]) Gildemeister and Hoffmann, *The Volatile Oils*, p. 312.
[3]) Report October **1890**, 67.

New Essential Oils.

Lebanon Cedar Oil. We have recently distilled a small quantity of genuine Lebanon cedar wood, and we are thus in a position to give some particulars of a really authentic oil from *Cedrus Libani* Barr. (*Pinus Cedrus* L.; *Abies Cedrus* Poir.; *Larix Cedrus* Mill.). At the same time we wish to place it on record that the particulars concerning Lebanon cedar oil which are to be found in our Report for April **1892**, 55, should be deleted as being inaccurate, since the distillate there described, as was shown by subsequent examination of the wood then worked up, was derived from a species of *Juniperus*, in other words, was not Lebanon-cedar oil at all. The authentic wood yielded about 3,5 % of a lemon-yellow oil of a pleasant balsamic odour, reminding at the same time of methylheptenone and of thujone. This oil possessed the following constants: $d_{15°}$ 0,9427, $\alpha_D + 80° 20'$, $n_{D20°}$ 1,51254, acid no. 0,5, ester no. 3,0 ester no. after acetylisation 19,8, soluble in 5 to 6 vols of 95 per cent. alcohol. It boils chiefly between 270 and 290°, the fractions passing over in an ordinary fractionating flask at 754 mm. being as follow: —

between	270	and 275°	30 %
	275	„ 280°	40 %
	280	„ 285°	14 %
	285	„ 290°	6 %
		Residue	10 %.

The chemical examination of the oil has already been taken in hand by another investigator.

Ifi-Ifi-Nuts. We desire to amplify the statements made in our last November Report[1]) with regard to the parent plant of ifi-ifi nuts by stating that Thiele, in his pamphlet *Über wirtschaftliche Verwertung ethnologischer Forschungen*[2]) designates this plant as being of the N. O. Leguminosæ and gives it the name of *Inocarpus edulis* Forst. (*Bocoa edulis*) while afterwards, in the *Chemiker Zeitung* he cited the parent plant as one of the Rosaceæ, viz., *Parinarium laurinum* (author?). Our previous communication was based upon the last statement. We incidentally learn from Samoa that only *Inocarpus* can be regarded as the source of ifi-ifi nuts.

At the same time we were informed that the flowers of this tree possess an exquisite odour, but that attempts which had been made locally to obtain an essential oil from them had been without result.

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[1]) Report November **1908**, 136.
[2]) Tübingen 1906, p. 37.
[3]) Chem. Ztg. **31** (1907), 629.

Pharmacopœias.

Suggestions for the new German Pharmacopœia, Ed. V.

The partial insufficiency of the indications of the present German Pharmacopœia on the subject of essential oils and their examination have induced H. v. Soden[1]) to make suggestions for the projected new Edition with the object of improving and enlarging the present prescriptions and bringing them in accord with the present state of knowledge. The expositions of v. Soden agree on the whole with our own views on the matter under discussion, as expressed by us in a letter to the Authorities concerned about $2^1/_2$ years ago. This applies especially so far as important general considerations are concerned: in details we may differ to some slight extent. It would therefore be superfluous on this occasion to go into details on the whole of v. Soden's paper, we will rather restrict ourselves to short references on matters in which there are discrepancies between v. Soden's findings and our own.

Calamus Oil. α_D: v. Soden $+$ 10 to $+$ 30°; Schimmel & Co. 9 to $+$ 31°.

Carvone. v. Soden: $d_{15°}$ 0,964 to 0,966; α_D $+$ 58 to $+$ 60°; Schimmel & Co.: minimum limits 0,963 and $+$ 57° respectively.

Cinnamic Aldehyde. $d_{15°}$: v. Soden 1,054 to 1,056; Schimmel & Co. 1,054 to 1,058 (from observations made on material prepared by ourselves).

Juniper berry Oil. $d_{15°}$: v. Soden 0,860 to 0,880; Schimmel & Co. 0,860 to 0,882.

Lavender Oil. v. Soden recommends that the minimum requirement of ester content be fixed at 33 to 35% in lieu of 30% as at present. In our opinion there is no particular reason for this demand.

Mustard Oil. v. Soden justly regards the incorporation of artificial mustard oil as necessary and he gives for this, as limits of value, a sp. gr. of 1,022 to 1,024. In the case of our own preparation these limits lie between 1,020 and 1,025. In order not to exclude the natural oil from medicinal use it would be necessary to specify a sp. gr. of from 1,014 to 1,025.

Nutmeg Oil. α_D: v. Soden $+$ 8°; Schimmel & Co. $+$ 7°.

Peppermint Oil. v. Soden: $d_{15°}$ 0,900 to 0,912; α_D $-$ 20 to $-$ 33°; gives a clear solution with 4 parts of 70 per cent. alcohol, the solution remaining clear when more alcohol is added. Menthylacetate

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[1]) Pharm. Ztg. **54** (1909), 249.

content 5 to 15 %, free menthol content 45 to 60 %. Schimmel & Co.: $d_{15°}$ 0,900 to 0,910; α_D — 23 to — 30°; total menthol 50 to 66 %. With 4 to 5 vols. *spir. dil.* peppermint oil should give a clear, or at most a slightly opalescent solution.

We expressly abstain from insisting upon an absolutely clear solution in dilute spirits, because even in the case of good English oils slight opalescence is occasionally noticeable.

As regards the menthol content it appears to us, in the case under discussion, to be more practical simply to state the total menthol percentage, i. e. the value resulting from saponification after acetylation. In doing so, it is true that no account is taken of the fact that part of the menthol occurs in the oil as an ester, but the values obtained are at most 2 or 3 % too high and will therefore be amply sufficient in practice. Separation into esterified menthol and free menthol would complicate the test needlessly.

v. Soden justly points to the difficulties which exist in estimating the quality of peppermint oil. He recommends either to lay down general constants and to admit all varieties of peppermint oil, or to incorporate only two kinds of peppermint oil, namely English oil on the one hand and all other kinds on the other. We only regard the first suggestion as acceptable, the other would doubtless be found to have many drawbacks. At the time we suggested to the Authorities concerned the advisability of admitting oil from *Mentha piperita* and from varieties of *Mentha* closely allied thereto in order to avoid as far as possible the difficulties that would otherwise crop up. Of course, if this were done it would be necessary so to fix the constants that the pharmacist would have a guarantee of receiving good oil.

Rose Oil. v. Soden: $d_{30°}$ 0,849 to 0,862; α_D — 1° 30′ to — 3°; Schimmel & Co.: $d_{30°}$ 0,849 to 0,863; α_D — 1 to — 3°.

Sandalwood Oil. v. Soden: $d_{15°}$ 0,975 to 0,980; α_D — 16° 30′ to — 20°; Schimmel & Co.: $d_{15°}$ 0,975 to 0,985; α_D — 16 to — 20°.

v. Soden proposes to fix the minimum content of santalol at 92 %, calculated for $C_{15}H_{24}O$. We should not like to endorse such a proposal, for according to our experience with our own distillates even oils made from the best materials occasionally contain a little less santalol that this. The commercial practice of requiring a minimum of 90 % is in our view the one most in harmony with facts.

v. Soden's recommendation to discard sandalwood oil in favour of santalol, we should certainly not be able to endorse, principally because of the increase in price which would thereby be made unavoidable for a medicament which is already rather expensive.

Chemical Preparations and Drugs.

Apiol. This preparation remains out of the market, as it has not been possible to procure the necessary raw material. The position as depicted in our last Report has therefore undergone no change.

Civet. We cannot too often insist on the fact that we have at our disposal an excellent assortment of civet in original horns, and that the civet business is a speciality of ours *par excellence.* It is notoriously difficult to judge the quality of the drug, and on account of its peculiar properties it is entirely an article which must be taken on trust.

Copaiba Balsam, Bolivian. C. Hartwich[1]), in a paper on Bolivian drugs, reports on a new Copaiba balsam of Bolivian origin. This balsam is not only of interest because it comes from an entirely new producing district, but also, and especially, because it is the product of a new and hitherto unknown species of copaiba.

This species, which was discovered by Herzog in Bolivia, and is described by him as *Copaiba paupera* nov. spec. is a tree about 30 meters high, which occurs sporadically in the forests of the Province of Velazco, on the Rio Blanco, and is known to the natives by the name of *Copáivo.* The balsam occurs in the heart-wood, in hardly visible channels, and in much smaller proportions than in the copaibas previously known. Herzog states that the balsam is obtained by cutting a hole in the tree in a downward slanting direction, reaching to the heart of the wood. The manner in which this is done is explained in the original article by means of an illustration. The exudation of the balsam continues two or three days, the total output per tree being about 11 kilos. The quantity of balsam at Hartwich's disposal was insufficient to admit of a complete examination, but the results obtained by him were as follow: —

The product was of a viscous consistency, light brownish yellow colour, and resembled the known varieties of copaiba balsam (especially Maracaibo balsam), both in odour and in taste. It also resembles the latter in its other properties, but in its optical behaviour it offers marked differences, being in this respect more nearly related to African balsam, for, like that variety, it is dextrorotatory, whereas all other copaiba balsams turn to the left. We give the constants below: $d_{15°}$ 0,998, $\alpha_{D\,15°}$ + 36°, $n_{D\,20°}$ 1,522, acid no. (according to Dieterich) 89,7, sap. no. (cold) 97,23, from which is calculated an ester no. 7,55; sap. no. (hot) 101,5. The higher value of the last-named figure agrees with the observations made by Utz[2]) on other

[1]) Schweiz. Wochenschr. f. Chem. u. Pharm. **47** (1909), 373.
[2]) Apotheker Ztg. **21** (1906), 205; Report October **1906**, 28.

copaiba balsams, while opposed to our own experience[1]). The balsam gives a clear solution with ether, chloroform, and petroleum ether. Excess of petroleum ether causes a whitish yellow, flocculent precipitate, while the highly diluted etherial solution is cloudy. It dissolves in absolute and in 95 per cent. alcohol with very slight opalescence, while if left to stand for a long time, a sediment forms. Liebermann's cholesterol test gives first a reddish violet and next a bluish-violet coloration, finally changing to violet grey. Dodge's and Olcott's test gives no coloration, while in the case of Turner's test[2]) the central layer assumes a brown colour.

By steam distillation the balsam yielded about 23 % of an oil with the following constants: $d_{15°}$ 0,916, α_D + 18°, $n_{D20°}$ 1,5048, acid no. 1,07, sap. no. (cold) 1,60. It is soluble in 9 vols. of 95 per cent. alcohol, as well as in ether, chloroform and petroleum ether. Liebermann's test gives at first a blue and then a green coloration; Flückiger's test a scarcely perceptible dirty colour. When the oil was fractionated under ordinary pressure, about 70 % passed over between 250 and 270° and about 10 % over 270°. Hartwich concludes from the constants that the principal fraction contains caryophyllene and cadinene, but he does not mention any experiments for identifying these bodies.

Eucalyptol is one of our most important specialities, in which we are able to defy all competition. The quality of our product is unequalled and all those who have not yet availed themselves of its advantages are strongly advised to try it. Our considerably reduced quotations show that we are prepared to maintain our leading position in this article.

Gurjun Balsam. The balsam (*Balao*) from *Dipterocarpus grandiflorus*, which was examined by Clover[3]) some years ago, has again been investigated by Bacon[4]). The balsam, when distilled under atmospheric pressure and *in vacuo* yielded an oil containing a mixture of crystalline acids, of which only a part was soluble in ether. In the fraction boiling at 128 to 131° (13 mm.) a sesquiterpene was also detected which, when distilled three times over sodium, appeared in the form of a colourless oil with the following properties: b. p. at ordinary press. 261 to 262,4° (standardized thermometer entirely immersed in the steam), 118 to 119° (8 mm.), $d^{30°}_{4°}$ 0,9104, $\alpha_{D30°}$ + 116,4°, $n_{D30°}$ 1,4956, ester no. and sap. no. 0, mol. refr. found 65,9, calc. for $C_{15}H_{24}/\overline{2}$ 66,15. The sesquiterpene, according to these data, was bicyclic and double unsaturated. Attempts to obtain clearly defined

[1]) Report April **1905**, 24.
[2]) Comp. Report April **1909**, 42.
[3]) Comp. Report April **1907**, 39.
[4]) Philippine Journ. of Sc. **4** (1909), A, 121.

derivatives of the sesquiterpene by means of bromine or hydrochloric acid gas, and to isolate definite products of oxidation by treating with permanganate failed, the latter experiment only yielding resinous bodies of aromatic odour. The terpene appeared to be sensitive to light to this extent that, after having been kept for 18 months in a stoppered glass bottle the rotation had fallen to $+101{,}2°$, the other constants being almost unchanged.

Ionone. In the American Journal of Pharmacy, S. P. Sadtler[1]) discusses the preparation, separation, characteristics, and physical properties of α- and β-ionone. We cannot altogether agree with the author's opinion that Tiemann's separation of the two isomerides by steam distillation of their bisulphite solutions is very satisfactory, for according to our experience this process gives rather inaccurate values, and in particular do we regard it as unsatisfactory to pronounce an opinion on the β-ionone contents of an ionone-mixture on the basis of results obtained by this method; for in the first place the ionone which has separated by steam distillation without addition of an alkali from the bisulphite solution of a mixture consisting for the greater part of α-ionone, is not pure β-ionone. It is of course presupposed that the distillation is continued until there is a pronounced foaming, which ultimately prevents its continuance. In the second place, when the bisulphite solution of a mixture consisting chiefly of β-ionone is distilled and strong foaming ensues, by no means all the β-ionone has passed over. It is possible after liberating the supposed α-ionone which has remained behind in combination, and after treating it repeatedly with bisulphite and subjecting it to steam distillation, to separate still considerable quantities of β-ionone. But even in the case of a mixture consisting chiefly of α-ionone it is possible, after treating it three or four times with bisulphite, to prove the presence of small quantities of β-ionone by subsequent steam distillation without the addition of alkali. Hence the investigator might be tempted to suppose that every time the bisulphite treatment was applied it effected the inversion of certain quantities of α-ionone into β-ionone. In making this statement we continue of course to presuppose that the steam distillation is continued to strong foaming. A further source of the inaccuracy of this method lies in the loss of oil, amounting to about 10%, which is caused by any bisulphite treatment of small quantities of ionone. In our opinion the method does give a guide for the estimation of the mutual relations of the two isomerides, but we consider it to be too unreliable for the determination of the percentage proportions of α- and β-ionone. In conclusion, the author, apparently influenced by the Patent law-suits

[1]) Americ. Journ. Pharm. **81** (1909), 181.

which have lately been heard in the United States, discusses Tiemann's first ionone patent of 1893 as well as those of 1896 and 1897 (U. S. A. Patents). He points out that as far back as the year 1897, that is to say before Tiemann's publication on the subject of the existence of α- and β-ionone in ordinary ionone[1]), the firm of Chuit, Naef & Co., of Geneva, had brought into commerce an ionone which differed somewhat from Tiemann's.

Irone. For the synthesis of this body see Orris Oil, p. 83.

Menthol see Peppermint Oil, Japanese, p. 98.

Musk, Tonquin. No recent information has come to hand concerning this article, the only news with regard to the coming season being that slightly lower prices are probable. In our next Report we will again be in a position to give detailed particulars on the course of the market, and to include statistical information as to the exports, which up to the present is not available.

Myrocarpus Balsam. This article is one of the obsolete balsam of medieval pharmacopœias. E. Schaer[2]) has had under examination a sample of it which had been handed down in a family. A comparison of the properties of this sample with the statements of ancient writers on Natural History confirms his surmise that the article is identical with *Cabureiba* Balsam, which was described by the Dutch physician Willem Piso about the middle of the 17th century in his *"Historia naturalis Brasiliae"* IV. **5**, 57, and also with that called *"Baume du Pérou en coques"* by Gibourt in his *"Histoire naturelle des drogues simples"*. From the two species *M. fastigiatus* Allem. and *M. frondosus* Allem. of the *Myrocarpus* family, which are natives of Central Brazil, there exudes, either naturally or as the result of incision, a balsam which is caught up in the hollowed-out, walnut-sized fruits of certain palms or myrtaceæ. After the contents have been left to dry for several days, the receptacle is closed with vegetable wax. The balsam itself is reddish brown, and apart from its viscous consistency it showed great similarity to Peru and Tolu balsam in its appearance and odour, as well as in its other properties. Among its constituents Schaer found both free benzoic acid, and benzoic acid in combination with aromatic alcohols. On the other hand, neither cinnamic acid nor vanillin could be definitely determined as such.

A sample of balsam which was sent to us a long time ago may also be a Myrocarpus balsam, as all the details given by Schaer agree precisely with our sample, which was moreover also contained in a fruit the size of a walnut, and sealed with wax.

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[1]) Berl. Berichte **31** (1898), 867.
[2]) Arch. der Pharm. **247** (1909), 176.

With regard to the oil obtained from the aromatic wood of *Myrocarpus fastigiatus* Fr. All., compare Gildemeister's and Hoffmann's *The Volatile Oils*, p. 447.

Peru Balsam. There is little to be said concerning the market position and the prospects of this article. The sluggish sale has caused the Hamburg importers to show a little more pliability during the last few months and several holders of important consignments are on the look-out for interested parties. It is quite impossible to hazard any opinion as to the probable course of prices during the coming months, because no information is procurable as to the extent of the production, the stocks in the producing districts, etc.

With regard to the solubility of Peru balsam in alcohol, the German Pharmacopœia, Ed. IV, only says that it is "clearly miscible with spirits of wine (90 to 91 per cent. by volume)". Although this indeterminate mode of expression, which leads to misunderstandings, has been frequently exposed in the pharmaceutical press[1]), yet claims on account of imperfect solubility of balsam supplied are made again and again from the ranks of the pharmacists. We therefore feel compelled to call attention to the fact that the requirements of the German Pharmacopœia, as quoted above, are in need of a correction in the form of amplification; for, although the concentrated alcoholic solution of Peru balsam (1:1) is clear, further addition of alcohol soon induces cloudiness, which increases in proportion to the extent of the dilution. Peru balsam which gives a clear mixture with spirits of wine in any proportion does not exist.

The obscurity of the prescription of the German Pharmacopœia Ed. IV is the more to be regretted, because the previous Edition (III) of that work correctly stated that 1 part of Peru balsam gives a clear mixture with 1 part of spirits of wine. In the commentary to the third Edition, edited by Hager, Fischer, and Hartwich it is, moreover, expressly pointed out that turbidity ensues when more spirits of wine is added, and that, when the diluted mixture is allowed to stand, a sediment is precipitated.

As regards the sp. gr. we may observe that, according to our experience, in the case of pure balsam this lies between 1,144 and 1,154 (15°), while the German Pharmacopœia Ed. IV, only allows 1,150 as the maximum sp. gr. In the interests of honest trade it must be remembered in this connection that the sp. gr. of most balsams exceeds 1,150. A sp. gr. of up to 1,154 should in no case be allowed to justify claims when the balsam concerned answers the Pharmacopœia requirements in other respects.

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[1]) Pharm. Zentralh. **44** (1903), 241; Pharm. Ztg. **48** (1903), 363, 754.
[2]) Second Ed., Vol. I, p. 390.

On the basis of numerous cinnameïne determinations made with samples of the best brands on the market, we are further in a position to state that the cinnameïne content even in the case of good balsams is occasionally as low as 55 %. The ester number of cinnameïne, which according to the German Pharmacopœia Ed. IV must be at least 236, varied from 232 to 242.

We cannot refrain from stating the fact that the best brands of balsam which are available in commerce, very often fail to come up to Pharmacopœia standard in one respect or another, while on the other hand balsams which answer the Pharmacopœia tests may be had without difficulty at low prices. Such an illogical state of things affords cause for reflection, and must involuntarily induce doubts as to the purity of the last-named balsams.

Pollantin. While the etiological connection between hay-fever and the pollen of certain plants, which has been revealed by the work of Dunbar and his collaborators, has been generally admitted even by the opponents of Dunbar's views on serum therapy, P. Bonnier[1]) in an article entitled *"Le rhume des foins"* denies the existence of such a connection, or at any rate maintains that the pollen is the cause of the affection in only very few instances. According to him, in the vast majority of cases the exciting agents are altogether different, consisting in fact, of certain powders, such as flowers of sulphur or rice powder, or of definite and in some cases external nervous irritants, including wind, the reflection of the sun, light etc., which have frequently no connection whatsover with flowering grass or with the hay crop. The symptoms caused by these agents are the same as those provoked by susceptibility to irritation from pollen. Bonnier traces them to disturbances in the equilibrium of the nerve-centres which regulate the secretive action and, in special cases, also of those which influence the action of the bowels, the separation of urine etc. In treating such cases, Bonnier thinks the application of specific serums has been of less effect than, maybe, the "neutralisation" of the centres in question by the gentlest and most superficial possible cauterisation of certain places in the mucous membrane of the nose.

Bonnier appears to have overlooked the whole of the voluminous literature on the subject which has been published during the last six years, or he would certainly not have overlooked the fact that almost all authors differentiate clearly between general secretory neuroses and hay fever *sensu strictiori*, that is to say an idiosyncracy founded on the susceptibility of some individuals towards the albumens of certain pollen. Before these had been recognised as being the causes of the periodical affection in question, — an affection which only attacks the

[1]) Compt. rend. **148** (1909), 1694.

same class of individuals, — both ailments were classed together under the general name of "hayfever". But since Dunbar's publications that name is given only to the complex of symptoms which is provoked by the effect of pollen on predisposed individuals, and removed by a specific serum. Bonnier, however, as will be seen, does not apply the expression *"rhume des foins"* in this, its only correct sense; he uses this term for both affections, in the old fashion, although their causes are fundamentally different. Bonnier would immediately recognise the great distinction between *Coryza nervosa* and true hay fever if he would amplify his theories by practice, test the excitability of a few of his patients by means of pollen extracts, and then proceed to remove any symptoms of excitation which may manifest themselves, with the specific serum.

The error into which Bonnier has fallen in his views on the treatment of "hay fever" is shown by the many reports which we receive, principally from Western Europe, and above all from England, of the excellent action of our Pollantin. To these reports must be added one which has just come to hand from a medical practitioner in Paris, who has experienced its beneficial effects on himself.

Safrol. Enormous quantities of this article continue to be sold, the United States especially showing strong interest in the preparation. We refer to the statements under camphor oil (p. 29), and will only add thereto that during the period under review no alterations in price have taken place.

Tannothymal. During the past year or so this preparation has been much used in the Veterinary Institute of Leipzig University in the treatment of diarrhœa in animals. According to a communication by Prof. A. Eber[1]), Director of the Institute, it has been found of particular service (in doses of 4 to 5 g.) against diarrhœa of calves, a complaint which, owing to change of food, often causes much trouble in animals acquired for experimental purposes.

Thymol. It has lately been noticeable that those Hamburg firms who have earned the doubtful distinction of having thoroughly ruined the trade in this article are no longer quite so persistent as formerly in undercutting every reasonable quotation, and it is to be assumed that they are at last growing tired of the practice. It is to be hoped that some understanding may be arrived at, which will make business in the article more satisfactory again in the future. That enormous quantities, both of thymol and of ajowan-seed, are available in Europe is evident from the fact that although the raw material has risen in price by about 25% during the past few months, the thymol quotations at present show no inclination to follow suit.

[1]) Deutsche tierärztl. Wochenschr. **17** (1909), 107.

Vanilla. Among the aromatic constituents of vanilla, vanillin is the most important one. Good varieties of vanilla contain about 2 % of vanillin, but the value of vanilla cannot be judged entirely by its vanillin content; the aromatics which accompany vanillin are also of great importance in determining the character of the aroma of vanilla. Up to the present hardly any attempts have been made to isolate these constituents and to investigate their properties. W. Busse[1]) surmises that the fruit of certain inferior varieties of vanilla, the so-called *vanillons*, as well as that of *Vanilla planifolia* Andr., which is cultivated in Tahiti, contains piperonal as well as vanillin. But up to the present no definite proof for this statement has been given.

In order to obtain further knowledge of the aromatic principles, other than vanillin, which are contained in Tahiti vanilla, we prepared an ethereal extract from 9,2 kilos of this vanilla, from which, after removing the vanillin by means of soda liquor, we obtained by steam distillation 7 g. of a pale brown oil with a pleasant characteristic odour.[2])

The oil was heavier than water; its b. p. lay between 105 and 118° (6 mm.). 6 g. distilled over at about the b. p. of anisic alcohol, 115 to 118° (6 mm.). Artificial anisic alcohol prepared from anisic aldehyde showed, at 5 mm., a b. p. of 117 to 118°. The fraction 115 to 118° of the vanilla oil contained, besides anisic alcohol, a little anisic aldehyde, of which the semicarbazone melted at 204°. With phenyl *iso*cyanate the fraction gave a urethane, m. p. 93°, which was identical with the urethane from artificial anisic alcohol. When the fraction was oxidised with permanganate solution anisic acid was formed, m. p. 180°. Free anisic acid was also detected in the alkaline extract of the vanilla extract. On the other hand, no piperonal could be discovered. We have not yet been able to determine whether anisic alcohol and anisic aldehyde are also constituents of the odoriferous principle of the more valuable Bourbon vanilla, but it is our intention to experiment in this direction with considerable quantities of raw material.

Vanillin. The French Government have received a memorial containing 2500 signatures, from vanilla planters in the French Colonies, urging the imposition of a sufficient excise-duty upon vanillin to enable the vanilla-producers, who describe themselves as struggling for their existence, to compete successfully with the artificial scent. As a result of this step it is intended to ask the French Parliament to sanction an increase in the import-duty on vanillin to frcs. 15 per kilo, in addition to an excise-duty of 60 frcs. per kilo. Six colonial Deputies,

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[1]) Arbeiten a. d. Kaiserl. Ges.-Amt **15** (1898—1899), 107.

[2]) H. Walbaum, Über das Vorkommen von Anisalkohol und Anisaldehyd in der Tahiti-Vanille. Wallach Jubilee Publication, p. 649 (Göttingen, Vandenhoek & Ruprecht, 1909).

chiefly from Réunion, are agitating with great zeal for the adoption of the proposal, and it will be a matter of great interest to watch whether it will be carried into law, or whether the French industries which consume vanillin will successfully oppose a scheme under which, in future, they would be deprived from the advantage of being able to employ the most important odoriferous substance.

In an article appearing in the *Parfumerie Moderne* quoted from *La Nature*[1]) the alleged toxicity of vanillin known as vanillism is discussed in connection with two cases which have recently been made known, in which persons who had been working with vanillin were affected by ulceration of the skin. The paragraph referred to also states that it must not be forgotten that vanillin is a methyl ether of protocatechuic aldehyde, and for this reason alone is not a harmless body. In cristicism of this allegation we refer to a statement by Kobert[2]) who, in proof of the harmlessness of vanillin, mentions the fact that in the vanillin-works of Haarmann & Reimer there has been no instance in the course of 18 years of any of the hands contracting illness through vanillin.

Notes on recent research work concerning terpenes and terpene derivatives.

General.

Under the title "Philippine Terpenes and Essential Oils", Bacon[3]) has published a continuation of his previous work on the same subject[4]). His references to already known oils are discussed under the essential oils in alphabetical sequence; our object here is to refer to the new distillates prepared by him.

Oil of *Pittosporum resiniferum* Hemsl. (Pittosporaceæ). This tree, which is widely spread throughout the Philippines but does not occur very frequently and grows at altitudes between 170 to 2500 ft. (mostly about 500 ft.), produces fruits which is known on account of its petroleumlike odour as "petroleum nuts". When a lighted match is held close to it, even the green fruit burns with a bright flame. An examination of the oil of petroleum nuts showed, as might have been surmised from the odour, the presence of heptane and of a dihydro-terpene. Heptane, as is well known, is almost the

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[1]) La Parfumerie Moderne **2** (1909), 50.
[2]) Kobert, *Lehrbuch der Intoxikationen*, 2. Ed. **1906**, II. 143.
[3]) Philippine Journ. of Sc. **4** (1909), A, 93 ff.
[4]) Report November **1908**, 128, 173.

sole constituent of the oil of *Pinus Sabiniana* Dougl.[1]). A testal sample of one kilo of green fruit yielded when pressed 52 g. of oil, and the residual cake after being ground and pressed again gave another 16 g. Its properties were: d 0,883, $n_{D30°}$ 1,4577. No other optical constants could be determined. The oil was very viscous, and when spread in a thin layer it resinified quickly. When set alight in an open dish, it burned with a smoky flame. Under distillation, it passed over without decomposition up to 165°, after which point a resin-like oil passed over under decomposition. The fraction which boiled over between 100 and 165° was colourless and had a lemon-like odour. Further fractionation resulted in a fraction boiling between 98 and 103° with the following constants: $d^{30°}_{4°}$ 0,6831, α_D 0, $n_{D30°}$ 1,3898. The 7th and last fraction, which had b. p. 155 to 160°, and a turpentine-like odour, showed $d^{30°}_{4°}$ 0,8263, $n_{D30°}$ 1,4630. Further quantities of petroleum nuts of various origin were worked for oil partly by pressing and partly by distillation after previous crushing, and the fractions boiling up to 165° were added together and fractionated. The result was as follow:

Fraction	1,	b. p.	97 to 101°,	203 g.
„	2,	„	101 „ 120°,	12 g.
„	3,	„	120 „ 130°,	8 g.
„	4,	„	130 „ 140°,	7 g.
„	5,	„	140 „ 150°,	14 g.
„	6,	„	150 „ 160°,	600 g.

Residue: A viscous resin which, when further distilled, yielded a pale and strongly acid oil.

Fraction No. 1, extracted with concentrated sulphuric acid and distilled over sodium, yielded 197 g. of oil with the following constants: $d^{30°}_{4°}$ 0,6752, α_D 0, $n_{D30°}$ 1,3840. The oil, which had an odour of diphenylmethane, is no doubt heptane; brominating led to n-heptyl-bromide, b. p. 178 to 181°, at 70 mm. 93°. This, boiled with fused sodium acetate and glacial acetic acid, gave n-heptyl acetate, b. p. 192°.

Fraction No. 6, distilled three times over sodium, finally boiled at 158 to 160°: $d^{30°}_{4°}$ 0,8252, $\alpha_{D30°}$ (+?) 29,6°, $n_{D30°}$ 1,4587. The liquid hydrochloride had b. p. 114 to 116° (34 mm.) $d^{30°}_{4°}$ 0,9343, $\alpha_{D30°}$ + 9°, $n_{D30°}$ 1,4655. Treatment of this chloride with magnesium and subsequent decomposition with water resulted in a hydrocarbon with the following properties: b. p. 168 to 170°, $d^{30°}_{4°}$ 0,8050, $\alpha_{D30°}$ + 1,1°, $n_{D30°}$ 1,4460. Judging from these data, the hydrocarbon was regarded

[1]) Report October **1906**, 64; April **1907**, 85; October **1907**, 76.

as hexahydro-p-cymene, — hence the hydrocarbon of the original oil was a dihydrogenated terpene. Treatment of the chloride with magnesium and benzaldehyde led, as in the case of limonene and phellandrene (q. v.) to a hydrocarbon which also possessed two more atoms of hydrogen; in addition, benzoin appeared.

16 kilos of very small, ground, fruit of another species of *Pittosporum*, *P. pendantrum* (Blanco) Merrill, which grows chiefly in the lowlands of the Archipelago, gave, when distilled, 210 cc. of oil. The oil had b. p. 153 to 160° and after washing with alkali liquor and distilling over sodium it behaved as follows: b. p. 155° to 160° (chiefly 157 to 160°), $d_{4°}^{30°}$ 0,8274, $\alpha_{D30°}$ (+ ?) 40,4°, $n_{D30°}$ 1,4620. This oil, therefore, seems also to consist mainly of the dihydroterpene of the petroleum nuts described above, without heptane.

Some time ago Power and Tutin[1]) described an oil from the fruit of *Pittosporum undulatum* Vent. which came from South Australia.

An unknown species of *Fagara* (Rutaceæ) from the Northern Provinces yielded upon distillation of the leaves small quantities of an oil containing limonene and probably also a limonene derivative; the latter could also be obtained from limonene by treating it with diluted alkaline solution of sulphate of copper. This combination, on which Bacon proposes to report subsequently, gave a crystalline body with phenylhydrazin.

A Mexican oil of *Fagara octandra* L. has been described by us previously[2]).

The leaves of *Clausena anisum-olens* (Blanco) Merrill (Rutaceæ), a tree which occurs freely in certain districts have a strong odour of anise, as is indicated by the name. Their alcoholic extract has a similar odour, and the leaves are probably used by the natives in the preparation of their brandies known as *anisados*. Commenting upon the statement by Busse[3]), who lays special stress upon the heliotrope-odour of the East African species *Cl. anisata* Willd., Bacon points out that this odour is not found in his species of *Clausena*.

Bacon has unsuccessfully attempted to obtain an oil, or even a flower water, by distilling a quantity of 40 kilos of the flowers of *Plumiera acutifolia* Poir. (Apocynaceæ), a tree which is frequently planted in cemeteries, and of which the flowers have a slight but clearly perceptible odour of Frangipani. Special experiments showed that the odorous principle was destroyed when heated even to 40°. Extraction

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[1]) Compare Report October **1906**, 65.
[2]) Report April **1905**, 82.
[3]) Report October **1904**, 101.

with petroleum ether boiling at a low temperature, and distillation of the latter in *in vacuo* yielded a gum-like extract of pleasant odour. Better results were obtained by maceration ("*enfleurage*") with paraffin oil.

The last report of Roure-Bertrand Fils[1]) also contains information concerning *Plumiera acutifolia* Poir., together with a coloured illustration of the flower.

While in the preparation of chemical compounds recourse is very often had to high temperatures, in the case of plants even the most intricate chemical processes are accomplished at low temperatures, but at high pressure, i. e., the osmotic pressure present in plants. In the opinion of G. Austerweil[2]), the importance of this factor has been too much neglected in our chemical operations. The researches of Barbier have shown that pressure is also a factor in the conversion of members of the terpene series, Barbier having demonstrated that linalool, when heated with acetic acid in an autoclave at 160 to 170°, is converted into geraniol[3]). In the author's view this process also takes place in the vegetable Kingdom. Austerweil, referring to Pfeffer's opinion that osmotic pressure is greater at the equator than at higher latitudes, records as in harmony with this view the fact that an oil of petitgrain which had been distilled at 44°45′ N. Lat. was poorer in geraniol (1 part geraniol to 5 parts linalool) than an oil distilled from plants grown at 20° S. Lat. in South America, the latter, according to Umney and Bennett[4]), containing 38% geraniol and 30% linalool.

We should like to add to this example the following footnote: As for the figures quoted, they can only be approximate, inasmuch as no exact method for separating linalool and geraniol is known. Further, the figures given by Umney and Bennett and cited by Austerweil refer, it is true, to a South American oil, but it was not specially stated that this oil was distilled at 20° Lat. But in the same table the composition of Paraguay petitgrain oil is given as 18,9% geraniol and 52,4% linalyl acetate! In further support of his theory, Austerweil adduces oil of lavender (erroneously calling the parent plant *Lavandula Stœchas* instead of *L. vera* D. C.), and maintains that English lavender oil from herb grown at 55° N. Lat. does not contain geraniol, while this substance *is* found in French oil from plants growing in about 45° N. Lat. In criticism of this statement we may say that no exact

[1]) Berichte of Roure-Bertand Fils, April **1909**, 33.

[2]) Compt. rend. **148** (1909), 1197.

[3]) We may observe that to accomplish this, no pressure at all is required, and that this conversion takes places when linalool is boiled with acetic acid.

[4]) Pharmaceutical Journal **72** (1904), 217; Report April **1904**, 74.

analyses of English oil are available, and that in our opinion it is not even proven that it actually contains no geraniol The author also mentions an experiment with pinene, which he heated under pressure to about 200° in the presence of an organic acid (unspecified) of high m. p. and of an indifferent gas (carbon dioxide). After cooling, the limonene which had been formed was distilled over with steam and the borneol isolated after saponification. This method of preparing borneol and limonene from pinene has long been known, and was the subject of a patent granted to Zeitschel[1]) in 1907. Anyhow the presence of an indifferent gas in Austerweil's process is new.

Bibliography.

The majority of the raw materials from which essential oils are prepared are pharmaceutical drugs which have been known and esteemed for centuries, and the knowledge of which is the domain of pharmacognosy. The progress of the last few decades in our knowledge of the structure and the general chemical behaviour of the constituents of drugs has enriched the science of pharmacognosy by a new branch, pharmaco-chemistry, and the principal achievements made in this region of knowledge have been collected by Oesterle in his *Grundriss der Pharmakochemie* (Manual of Pharmaco-Chemistry), published Berlin 1909, by Gebr. Borntträger. This very welcome volume, which embraces the literature of the subject up to about the autumn of 1908, contains five principal sections, arranged according to the nature of the active principles of the drugs, viz., alkaloids, odoriferous substances, glucosides, dyes (or rather constituents yielding colouring materials) and tanning materials. These sections contain an exposition of the chemical behaviour of the bodies belonging to each particular division, classified according to the names of the drugs. The author admits that this arrangement is unsatisfactory in many cases, as, for instance, when a drug contains both an alkaloid and essential oil, as does pepper. More than one-half of the 530 pages of the work is occupied by the section dealing with drugs containing odoriferous constituents, such as essential oils, vanillin, coumarin, etc. Animal drugs are not considered. The arrangement of details is the same as that of the oils in Otto's book, which we discuss hereafter. First come the oils which contain hydrocarbons as their characteristic constituent and the drugs of which the oil contains the same leading constituent (*Ol. Terebintinae; Fruct. Phellandrii*, etc.) and next those of which the oil contains alcohols, (*Fruct. Coriandri, Fol. Menthae, Ol. Rosae*, etc.) aldehydes (*Cort. Cinnamomi zeyl.*, etc.), ketones, phenols and phenol-ethers, oxides, cumarin or damascenin. At the end comes *Rhizoma*

[1]) Germ. Pat. 204163, Chem. Zentralbl. **1908**, II. 1751.

filicis, of which the essential oil, although not particularly described, may yet be regarded as a somewhat insignificant active principle compared with its other constituents. As a result of the arrangement, bitter almond oil and its congeners, as well as wintergreen oil and the mustard oils are placed under the drugs containing glucosides. A general introduction at the beginning of each of the five sections gives indications as to the detection, isolation and identification of the various bodies, such as alkaloids, essential oils, etc., and mentions the principal analytical methods. Each constituent of an oil is treated with great thoroughness as regards its constants, general chemical behaviour, the more important conversions (especially its relations to other compounds known to occur in essential oils) as well as, where possible, its synthesis. The text is rendered still more complete by numerous chemical formulae graphically shown and by references to literature.

In the series known as the *"Sammlung Goeschen"*, published by the Leipzig firm G. J. Goeschen, a booklet of 190 pages (bound 0,80 marks) has made its appearance which, within the restricted compass prescribed for the series, treats of Essential Oils and Odoriferous Substances. (*Ätherische Öle und Riechstoffe.*) The author, F. Rochussen, deals in each chapter, after an historical introduction, with the mode of preparation and the properties of the oils, their phyto-physiological significance, their examination, and their adulteration. In the account of the more important oils and perfumes, which follows next in order, the raw materials and their occurrence are described, in the case of the oils also the separate constituents so far as they are known, and the properties, use, and tests of the products. The physical and chemical constants quoted are those which have been observed in our laboratory. The concluding part of the little volume, which is intended as an introduction and guide to the subject mentioned in the title, consists of a chapter on the use of oils and odoriferous bodies in perfumery and soap-manufacture, medicine, and arts, the manufacture of beverages, flavouring extracts, etc. We can warmly recommend this clearly written, concise booklet to all who desire to obtain a quick and accurate insight into our present knowledge of the essential oils and odoriferous bodies, as well as into their multifarious uses.

Under the title *A working List of the flowering Plants of Baluchistan*, Mr. J. H. Burkill has published a book (Calcutta, Superint. Govt. Pr., 1909), containing a list of the phanerogamous wild plants of Baluchistan. In addition to an enumeration of the scientific and vernacular names of the plants, the book contains many interesting

notes on their distribution, use and medicinal properties. A number of cultivated plants are included because the geographical limits of their distribution afford an indication of the climatic zones of the region.

The flora of Baluchistan has a somewhat northernly character, many genera indigenous in Central Europe, such as the violet, the primula, the whitethorn, the anemone, the gentian, and the juniper being represented.

L'industrie des parfums, d'après les theories de la chimie moderne, is the title of a work on essential oils and odoriferous substances by M. Otto (H. Dunod and E. Pinat, Paris 1909) on which we propose to make a few observations. The book is divided into four principal sections. The first two chapters of the first part contain an account of the fundamental principles of modern organic chemistry: the quadrivalency of carbon, the nature of the various linkings of carbon atoms, stereo-chemistry etc., followed by a general description of the different classes of bodies, for instance those hydrocarbons, alcohols, aldehydes, ketones, etc. Both these chapters may perhaps be regarded as superfluous in a work of this class, as their subject-matter is to be found in every text-book of chemistry and is, in fact, common property. In the next following chapters Otto considers the classification of the essential oils from the different points of view from which they may be subdivided. In this classification the author has adopted the system of division according to the chemical character of the leading constituent of the oils (a system which is in many respects open to criticism), and this notwithstanding the fact that he makes use (without acknowledgment) of the table from Gildemeister's and Hoffmann's book *The Volatile Oils* in which the oil-yielding plants are classed according to the Engler's system. Then come chapters on the physical and chemical examination of the oils and the detection of adulterations. The second principal section deals in the first place with the preparation of essential oils by distillation, extraction, etc., and, next in order, with the oils themselves. Under the last-named heading are included numerous representations of the apparatus and subsidiary appliances in use. These illustrations are partly taken from our Reports and from Gildemeister's and Hoffmann's book, and partly (chiefly in the case of the odoriferous substances) from the designs of the author himself, whose reputation in this particular branch is of the highest. There are also maps (likewise taken from us), which add considerably to the lucidity of the chapter. In the case of each oil there is a brief note giving the names also in German and English, the origin and the mode of production, physical and chemical constants, composition and tests, together with the adulterations practised and tests for their detection. In the case of odo-

riferous bodies (both those which are constituents of oils and those which are artificially prepared, chemically homogeneous, odoriferous substances,) details are given of their occurrence in nature or their mode of preparation by artificial processes. These notes are generally fuller than those given for the oils. The properties, the principal conversions, etc., are then dealt with. At the end of the book there is a set of tables of atomic weights, densities, boiling points, etc., in the case of which an indication of the sources would have been desirable, and a number of prescriptions for the preparation of perfumes In our estimation the details supplied concerning the essential oils might have been fuller. Compared with similar particulars given for odoriferous bodies they are a little bare, and the author, in many instances, might are well have acknowledged the sources of his information. Here and there we find antiquated formulæ, such as the 1,4-oxide formula for cineol instead of the 1,8-formula, a camphor formula with a tetracyclic ring, after the manner of pinene, and the formula of a primary alcohol for linalool. In the next place we feel bound to enter a protest against the assumption of the author, as expressed both in his preface and in his exordium, that the chemistry of odoriferous bodies, and, in fact, modern chemistry generally, is essentially a French science, based in one respect upon the teachings of French scientists (Lavoisier, Pasteur, Berthelot, Friedel and others), and in another upon the riches of the flower industry of Southern France. The most important work, theoretical as well as practical, in the domain of the odoriferous substances has been done by German chemists. We need only mention such names as Wallach, von Baeyer, Bredt, Tiemann, and Semmler, and, last but not least, the chemists of the great German essential oil factories. Men of other nations also, among them especially Englishmen and Russians, have participated with much success in the research work in this field. The haughty saying of Würtz *la chimie est une science française* may have had some justification at the time when the young chemist received his scientific consecration in the laboratories of Dumas, Pelouze, Péligot, and others, but nowadays it can no longer be said to hold good, as a glance through German chemical literature and German chemical industry shows. An unconscious acknowledgment of German work is to be found in the mention of the discovery of muskone, which occurs in conjunction with this glorification of French science.

H. Dunod and E. Pinat, Paris, also publish a volume of 610 pages by Paul Hubert entitled *Plantes à parfum,* which appears as one of their *Bibliothèque pratique du Colon* series.

This book is divided into three parts. In the first the author begins with a short review of chemistry in general and the chemistry

of terpenes in particular, after which he describes in detail the various modes of preparing essential oils as well as allied products, such as powders, soaps, extraits, etc.

In the second, and larger part of the book, Hubert discusses the principal colonial products which contain essential oil. In the case of almost every one of these he gives a historical survey and a short botanical description of the original plant, after which he proceeds to discuss its geographical distribution and cultivation, the collection of the drug, its preliminary preparation and its shipment. He also deals with the preparation, properties, prices and adulterations of the oil, and gives occasional prescriptions for the making of perfumes, sachets, etc. Generally speaking, but little attention is given to the testing of the oils. Numerous good illustrations help considerably towards the elucidation of the text, and the book, which has evidently been written in a painstaking manner, is likely successfully to fulfil its purpose of serving as a guide for the colonist.

It is not our intention to dwell on occasional inaccuracies which have slipped in here and there in the description of the properties of oils, as these details, as already stated, play but a subordinate part in the book. But we cannot refrain from mentioning another matter which we have observed while perusing the volume. It is a striking coincidence that, although M. Hubert repeatedly quotes his sources of information, he does not so much as mention the name of the book *The Volatile Oils*, written by Gildemeister and Hoffmann under our auspices, although this book has rendered M. Hubert excellent services in the compilation of his own work. The historical introductions to the various articles in particular, have mostly been appropriated almost sentence by sentence from the French Edition of *The Volatile Oils*. It is true that the sentences have mostly been re-cast slightly and that here and there one has been omitted, but the source is quite evident. In order to prove our contention we quote below some pages in which the "borrowing" is particularly obvious, the corresponding pages in Gildemeister's and Hoffmann's book (French Edition) being added in brackets: 207 to 209 (442 to 444), 237 (595), 242 (310), 252, 253 (391, 392), 291 (636), 306 (538), 424 (411), 439, 440 (553 to 556), 446 (558), 457 (566).

It is surely very singular that so copious a use of a source of information should have remained unadmitted. We are of course pleased when the merit of our publications is recognised by their being quoted in other books, but we have a right to expect that where this is done the source of origin shall be acknowledged, inaccordance with the general literary custom.

A book published by J. H. de Bussy of Amsterdam, entitled *Nieuw Plantkundig Woordenboek voor Nederlandsch-Indië*, by F. S. A. de Clercq

(edited after the author's death by Dr. M. Greshoff), contains principally a list of all the popular names (so far as they are known), in the native languages of the plants of the Dutch-Indies. With every name there is a reference to an alphabetical register of the scientific denominations, the latter containing in each case, in addition to the native names, interesting botanical, ethnographical and medicinal details, even gastronomical and other curiosities. It is very evident from the mass of facts presented that the natives possess keen powers of observation for the flora which surrounds them.

New continuations have appeared of the monographs by I.W. Brandel [1]) on the publications in the domain of essential oils. These continuations deal with the progress made in the years 1901 to 1903 [2]). The work has been referred to by us on several occasions.

Analytical Notes.

For the volumetric estimation of constituents of oils, such as eugenol, thymol and cinnamic aldehyde, F. X. Moerk [3]) recommends the use of the centrifugal apparatus, by which the troublesome adhesion of oil to the sides of the vessel is avoided, and a better separation of the undissolved oil is obtained. In his experiments, Moerk used a Babcock milk and cream bottle. After being extracted the mixture was centrifugalised. At from 800 to 1000 revolutions per minute the separation of the oil from the aqueous solution was completed in from 8 to 10 minutes. Moerk experimented with oils of clove, pimento, thyme, and cassia, and also carried out comparative tests exactly as laid down by the U. S. Pharmacopœia.

It was remarkable that, without exception, all the determinations made with the centrifugal machine gave higher values than the other, while, owing to the more thorough separation of the oil from the aqueous solution, the reverse might have been expected. It is true that no proof can be given of the accuracy of the figures, for, apart from the use of the centrifugal machine, Moerk's other tests have not been made under equal conditions. For the cinnamic aldehyde determination he used in one case a solution of neutral sulphite, but for the comparative tests carried out according to the U. S. Ph. he employed a bisulphite solution. In the latter case he found over 5 % less of aldehyde. In comparative tests we ourselves have only very rarely been able to ascertain differences exceeding 2 %, but we have always obtained the higher values with bisulphite.

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[1]) The Midland Drugg. and Pharm. Review **43** (1909), 110, 248, 326.
[2]) Report April **1908**, 168; November **1908**, 155; April **1909**, 110.
[3]) Americ. Journ. Pharm. **81** (1909), 327.

The phenol determinations also give different results for the comparative tests, but here Moerk used in one case a 10 per cent. and in another a 5 per cent. (U. S. Ph.) liquor. This, of course, must produce differences in the results. In the case of oils containing eugenol a 10 per cent. solution is useless in any case, because it also dissolves a portion of the non-phenols. Even a 5 per cent. liquor gives too high results in the cases of pimento oil, terpeneless bay oil and clove oil of high percentage, and for the same reason. Hence we have lately used a 3 per cent. liquor for such determinations. On the other hand, for thyme oils a 5 per cent. liquor is to be preferred. Some considerable time ago we entered at length into this question, and we may now refer to that publication[1]).

G. R. Pancoast and W. A. Pearson[2]) write on preliminary tests for the determination of the purity of essential oils. Among these they class tests for odour, taste, colour, and solubility, giving further details for the oils most in use. A reference to the paper will suffice here.

The method of J. Walther for the determination of the citral-content of oil of lemon by the aid of hydroxylamine, mentioned in our last Report[3]), which has been tried in a modified form with pure citral and oils of lemon by A. H. Bennett, has been submitted by us to a controlling test, Bennett's method is again described concisely below:

A mixture of 20 cc. oil of lemon (in order to avoid a calculation in the determination of the percentage we used 20 g.), with 20 cc. alcoholic (80 per cent. alcohol) semi-normal hydroxylamine-hydrochloride solution is diluted with 8 cc. alcoholic normal potash liquor and 20 per cent. of strong alcohol free from aldehyde, and boiled half an hour with a reflux condenser. When cooled, it is diluted with 250 cc. water and the hydrochloric acid which still remains in the form of hydroxylamine hydrochloride is neutralised, phenolphthalein being used as indicator. The hydroxylamine which is not combined with citral is now estimated volumetrically with semi-normal sulphuric acid by determining the final reaction by means of stipple-tests in a highly-diluted solution of methylorange. A similar course is adopted in a blank test without oil of lemon, in order to determine the volume of the hydroxylamine solution. From the difference in the cc. of semi-normal sulphuric acid used up in the two tests, the quantity of hydroxylamine which has entered into the reaction is obtained and thence, and by multiplying with 0,076, the citral-content.

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[1]) Report April **1907**, 118.
[2]) Amer. Perfumer **4** (1909), 65.
[3]) Report April **1909**, 110.

The object of our investigations was in the first place to determine whether hydroxylamine hydrochloride is suitable for the quantitative determination of aldehydes, especially of citral. For this purpose, aldehydes of known constitution were taken, viz.,

1. Several samples of pure citral prepared by ourselves, including citral from oil of lemon, the content of which by the use of neutral sodium sulphite was ascertained at 99%.

2. Solutions of acetic aldehyde, of which the aldehyde-content was ascertained at 50% by titration with sodium bisulphite and iodine solution.

3. Freshly distilled chlorine-free benzaldehyde, b.p. 178,5° (751 mm.) of which the purity was also shown by the clear solution with water made by its bisulphite compound.

The values determined according to Bennett were, for

Citral	88 to 93%	in lieu of	99%	diff. about	9%	compared with 100 per cent. aldehyde
Acetaldehyde	44 „ 45%	„ „	„ 50%	„	„ 11%	
Benzaldehyde	92 „ 93%	„ „	„ 100%	„	„ 8%	

The figures found were therefore about 10% too low. The citral-content of various terpenes from oil of lemon and oils of lemon was also determined, and known quantities of pure citral admixed to the samples. The citral-content was then ascertained afresh, and again found to fall about 10% below the values calculated.

Lemon-oil terpenes:

0,25%	citral-content,	+ 5%	citral	gave	4,85%	= 4,6%	instead of	5%
0,6%	„	+ 5%	„	„	5,2%	= 4,6%	„	„ 5%
1,2%	„	+ 5%	„	„	5,5%	= 4,3%	„	„ 5%

Lemon oil:

3,9%	citral-content,	+ 3%	citral	gave	6,5%	= 2,6%	instead of	3%
4%	„	+ 4,4%	„	„	7,8%	= 3,8%	„	„ 4.4%

Although it was made clear beyond doubt that Bennett has improved Walther's method, the above experiments show that even the improved method does not furnish exact results, as the values found averaged about 10% too low, calculated for citral present. The error probably does not matter very much in the case of oils of lemon, with their comparatively low citral-content, and the determination may therefore suffice for practical purposes, especially as it is easily carried out. But where oils of high percentage (lemongrass oil) are concerned, the error will naturally be much greater, and for such oils, therefore, Bennett's method does not appear to be admissible.

In our last Report [1]) we discussed a process described by A. G. Woodman and E. F. Lyford for the colorimetric determination of benz-

[1]) Report April **1909**, 111.

aldehyde. W. Denis and P. R. Dunbar[1]) have now published another method intended to serve the same purpose. In this process 10 cc. of the extract of almonds are mixed with 10 to 15 cc. of a freshly-prepared 10 per cent. phenylhydrazin solution, the liquid shaken, tightly closed, and left to stand in the dark for about 12 hours. Next, 200 cc. of cold water are added, and filtered through a Gooch filter-crucible. The precipitate is washed first with cold water and afterwards with 10 cc. of 10 per cent. alcohol, dried for three hours *in vacuo* at 70 to 80°, and weighed. The weight found, multiplied by 5,408, gives the number of grammes of benzaldehyde in 100 cc. of the solution. Benzoic acid or nitrobenzene have no disturbing effect upon the accuracy of the method.

The comparative investigations of H. Runne[2]) into the determination of hydrocyanic acid in bitter almond water supply a very valuable review and literary index relating to the methods of hydrocyanic-acid determination at present known. From Liebig's first method[3]) onwards up to the recent colorimetric tests of E. Durieu[4]), all methods of analysis by weight or volume, together with the suggestions for improvement made in the case of each method, have been checked and are critically discussed by Runne. The author finds Denigès' modification of Liebig's precipitation method to be the most useful and trustworthy test for bitter almond water. Denigès'[5]) modification consists in using iodide of potassium as an indicator instead of chloride of sodium, as proposed by Liebig, because the silver-salt of iodide of potassium is insoluble in ammonia, and it is thus made possible to carry out the decomposition of the cyanohydrin by the excess of ammonia instead of by potash liquor. In this process the termination of the reaction is shown by turbidity, caused by the iodide of silver eliminated, this being more readily noticed in the titrating liquid (since that is already more or less cloudy by itself), than either cyanide or chloride of silver, such as is separated in the original method. By this modification another drawback of Liebig's method is overcome, viz., that owing to the ready solubility of cyanide and chloride of silver in the ammonia which is formed by the decomposition of hydrocyanic acid it is possible that more silver solution may be used up than is accounted for by the actual content of hydrocyanic acid.

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[1]) Journ. Ind. and Eng. Chem. **1909**, p. 256. Through Chem. Ztg. Repert. **33** (1909), 281.

[2]) Apotheker Ztg. **24** (1909), 288, 297, 306, 314, 325, 333, 344, 356.

[3]) Liebigs Annalen **77** (1851) 102.

[4]) Bull. Soc. pharm. **1902**, no. 5.

[5]) Compt. rend. **117** (1893), 1078.

Vielhaber's method[1]) in which magnesium hydrate is used for splitting-up up the cyanohydrin, and chromate of potassium as an indicator, is also, as Runne shows, a thoroughly trustworthy one; but the preparation of the hydrate of magnesium (a body which loses some of its strength by keeping and by the absorption of carbon dioxide gas), is perhaps a little too cumbersome to make the process generally popular. It has however been incorporated into the U. S. Ph. for the determination of the hydrocyanic acid content of oil of bitter almonds, and in our laboratory, too, it has yielded the best results in testing oils containing that acid.

The same subject is dealt with in a paper by G. Guérin and L. Gonet[2]) which relates especially to Buignet's process[3]). Buignet's process agrees generally with the older method of C. Mohr[4]), and also shares its faults. According to both, sulphate of copper is added to an ammoniacal solution of hydrocyanic acid so long as the blue colour persists, in other words, so long as an excess of copper salt is present. But the blue colour is so faint that it is difficult to determine exactly when the reaction has reached its close. Guérin and Gonet recommend a slight addition (0,5 g.) of sodium sulphite to the ammoniacal hydrocyanic-acid solution, whereby the liquid which has titrated out is said to acquire a brighter and more intense colour. They are, moreover, of opinion that the copper-deposit which is precipitated contains more copper than is accounted for by Buignet's equation.

$$CuSO_4 + 4NH_4CN = (NH_4)_2SO_4 + Cu(CN)_2\,2NH_4CN$$

Hence, they argue, if 1 cc. = 0,001 g. HCN, the copper solution should contain not 23,09 g. but 30,81 g. of copper sulphate crystals per liter. According to the authors, the reaction takes place as follows:

$$CuSO_4 + 3NH_4CN = (NH_4)_2SO_4 + Cu(CN)_2NH_4CN$$

It remains to be seen whether the new suggestions will make the method more popular.

J. C. Umney[5]) has dicovered that the by-product in the manufacture of terpineol which is brought to market under the inappropriate name of Terpinolene is being used as an adulterant, especially of oil of spike. According to Umney, it is a particularly objectionable addition, because it does not noticeably influence the constants of spike oil, but must be principally detected by its odour, and its presence is therefore liable to escape an analyst who is not quite familiar with the characteristic odour of spike oil. When the spike oil is subjected to fractional distillation the adulterant is found in the parts

[1]) Arch. der Pharm. **213** (1878), 408.
[2]) Journ. de Pharm. et Chim. VI. **29** (1909), 234.
[3]) Ibidem III. **35** (1859), 168.
[4]) Liebig's Annalen **94** (1855), 198.
[5]) Chemist and Druggist **75** (1909), 292.

boiling over between 185 and 195° which thereby, in contradistinction to pure spike oil, acquire a particularly pungent camphor-like odour. The detection of a sophistication of this kind leads Umney to denounce in strong terms the practice which has recently been adopted by certain manufacturers of placing upon the market products which by their very nature can only be used as adulterants. Among such bodies, Umney mentions glycerin triacetate and triethyl citrate.

While we cordially range ourselves at Umney's side in his protest against such fraudulent practices, we cannot class this so-called terpinolene among the articles which he denounces, because it is justified in its existence as a bye-product in the manufacture of terpineol, and is much in request as a cheap scent for soaps. Its occasional use as an adulterant doubtless does not lie in the intention of the manufacturer.

The case is different, however, as regards the two other preparations named, which constitute very dangerous adulterants. But even here it does not do, perhaps, to condemn the preparation and sale of such preparations straightaway, seeing that some of them may also serve other purposes, even in the perfumery industry. But all those whose interest lies in maintaining honest trading in essential oils should decidedly oppose the altogether scandalous practice of publicly offering such esters for purposes of adulteration. We have by chance come into the possession of a circular letter from an Amsterdam firm which falls under this category. It is addressed to distillers of lavender oil and recommends a product of this kind (of which a small sample is added), for "raising the ester-content of the oils". Such a direct attempt at instigating the distillers to commit fraud ought properly to be made the subject of a prosecution.

On the separation of allyl and propenyl compounds, see p. 204.

On the testing of the camphor-content of spirits of camphor, see p. 33.

On the detection of indol and skatol, see p. 213.

On the determination of petroleum in oil of turpentine, see p. 125.

On the detection of small quantities of oil of savin, see p. 111.

Physical Notes.

Von Rechenberg[1]) has recently called attention to a source of error in determinations of boiling points under reduced pressure which had thus far escaped attention.

In determining boiling points or in distilling operations under diminished pressure the manometer is usually inserted between the receiver and the pump, at some considerable distance from the distilling-vessel.

[1]) Journ. f. prakt. Chem. II. **79** (1909), 475. (Communicated from the Laboratory of Schimmel & Co., Miltitz nr. Leipzig.)

In doing this, it is tacitly assumed that while the distilling is going on the pressure in the still is exactly that shown by the manometer. But this is only very rarely so; almost invariably the pressure in the distilling vessel is a few millimeters higher, consequently the reading of the pressure is almost always inaccurate and does not correspond with the temperature indicated. The reason of this is that the efflux-tubes of the distilling vessels are generally so narrow that the steam formed in the process of distillation is unable to escape quickly enough, as a result of which an excess of pressure is caused in the still. The extent of this excess of pressure depends partly upon the force of the distillation (i. e. the volume of steam which is generated within the unit of time), and partly upon the diameter of the efflux-tube, and is commensurate to the speed of the steam, i. e. to the rate of the volume of steam which is passed through the efflux-tube per second in proportion to its diameter. For the purpose of experimentally ascertaining the excess of pressure, water was distilled from a copper cylindrical still of about 25 liters capacity under reduced pressure. The still was connected with a manometer and the receiver with another manometer, so that the difference in the readings of the pressure indicated the excess of pressure in the still. By inserting glass tubes into the efflux-tube and by altering the force of distillation, the rate of velocity of the steam in the efflux-tube and consequently the excess of pressure in the still could be increased as desired. In the case of water. the following figures were found, calculated from the known (variable) diameter of the efflux-tube and the quantity of the distillate: —

Rate of velocity of steam 1 m. = 0,5 mm. excess of pressure
" " " " " 2 " = 1 " " " "
" " " " " 6 " = 2 " " " "
" " " " " 12 " = 3 " " " "
" " " " " 22 " = 4 " " " "
" " " " " 34 " = 9 " " " "
" " " " " 49 " = 12 " " " "

These relationships between excess of pressure and velocity of steam enable us to calculate the extent of the former in a boiling flask of from 50 to 100 cc. capacity, with a tube of 5 mm. width at a distilling-speed of 0,015 g. per second: —

	Distillation pressure	Temperature	Rate of velocity of steam	Excess of pressure
Water	760 mm.	100°	1,2 m.	0,5 mm.
"	50 "	38,3°	16,5 "	3 to 4 "
Pinene	760 "	159,2°	0,2 "	0 "
"	5 "	22,3°	20,7 "	3 " 4 "
Oleic acid	4 "	199°	20 "	3 " 4 "

In the case of bodies with high boiling-points (200° and over) an incorrect observation of the steam-pressure may equal a mistake of from 3 to 5° in the determination of the boiling-point; the simplest way of reading accurately, as pointed out by von Rechenberg, is to connect the boiling-flask directly with the manometer.

The author also explains that in the distillations in an exceptionally high vacuum which have recently been carried out by Fischer and Harries[1]) and by Krafft[2]) an incorrect pressure has been assumed as a result of the improper arrangement of the apparatus, as described above. Krafft even went so far as to talk of distillation at 0 mm., as he calls the vacuum of about 0,001 mm. Apart from the excess of pressure existing in the vessel, a distillation at 0,001 mm. would of itself be an impossibility (as may be shown by a simple calculation) because the steam would be so rarified that no observable distillate would be obtained. For instance, at a pressure of 0,001 mm. the quantity of material which would distil over from a distilling-vessel with an efflux-tube of 8 mm. width, at a distilling-speed of 0,1 m. would be 1 g. in 44,7 hours! Moreover, steam which was rarefied to such a degree would not even be capable of maintaining the glass and the mercury of the thermometer at steam temperature, and all the steam would be condensed by the thermometer. In any case where boiling points are being taken, or distilling is conducted under reduced pressure, the entire flask should be immersed in the heating-bath, because otherwise too much of the condensate runs down the inner side of the flask.

The Chemical Action of Light. If menthone in an aqueous-alcoholic solution is exposed for a long time to the action of light, it is hydrolytically split up (as observed by Ciamician and Silber)[3]) and a decylic acid, together with an aldehyde which is an isomeride of citronellal is formed. At the time the authors regarded this aldehyde as identical with the mentho-citronellal described by Wallach. Further investigations into the constitution of the aldehyde by the two authors[4]) were designed to find an answer to the question which of the two following formulæ applies to it:

I. $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C:CH\cdot CH_2\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot CHO$

II. $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH\cdot CH:CH\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot CHO$

[1]) Berl. Berichte **35** (1902), 2158.

[2]) Berl. Berichte **28** (1895), 2583; **29** (1896), 1316 and 2240; **33** (1900), 3217; **36** (1903), 1690, 4339, 4344; **40** (1907), 4775, 4779.

[3]) Berl. Berichte **40** (1907), 2419; Report October **1907**, 123.

[4]) Rend. della R. Accad. dei Lincei **18** (1909), 317. From a copy kindly sent to us; Berl. Berichte **42** (1909), 1510.

With this object in view the aldehyde was first converted into its hydroxamic acid (described at the time) and this acid hydrolysed by boiling with dilute sulphuric acid. If the aldehyde were really menthocitronellal of formula I the acid thus obtained should be identical with the menthonenic acid[1]) prepared by Wallach:

$$(CH_3)_2 \cdot C : CH \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CO_2H$$

The analysis of the acid prepared by the authors agreed with the formula $C_{10}H_{18}O_2$, the acid's b. p. was between 248 and 253° (760 mm.) or 142° (18 mm.), while Wallach's acid had b. p. 257 to 261°.

In order to determine the position of the double linking, it was oxidised with permanganate of potassium and afterwards with bichromate of potassium and sulphuric acid, β-methylglutaric acid (m. p. 86° from benzene) and (probably) *iso*-butyric acid being obtained as products of oxidation. This behaviour agrees with the formula:

$$(CH_3)_2CH \cdot CH : CH \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CO_2H \longrightarrow$$

$(CH_3)_2CH \cdot COOH$ — *Iso*-butyric acid

$COOH \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot COOH$ — β-Methyl glutaric acid

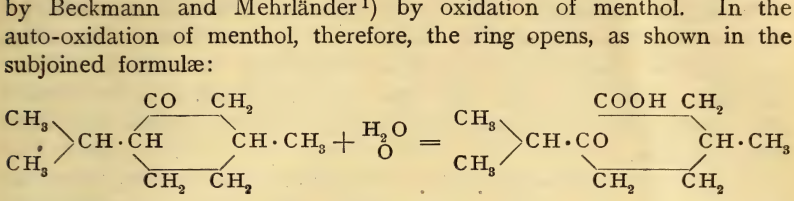
The constitution of the aldehyde might thus be regarded as being disclosed, but (as Wallach informed the authors by letter) it must be borne in mind that in certain circumstances, in the course of the process of oxidation with alkaline solution of permanganate the double linking may be displaced against the carboxylic group[2]).

In the same paper, Ciamician and Silber report on the auto-oxidation of menthone which occurs on exposure to light and in the presence of oxygen. 35 g. of menthone, together with water, were exposed to light for $3\,^1/_2$ months in large bottles of a capacity of 4,5 litres, filled with oxygen. At the end of this period the pressure in the bottles was greatly diminished, and the precipitated liquid had a pronounced acid reaction. Another bottle with similar contents, which had been left in the dark, showed hardly any change in pressure at the end of the same period. The non-acid parts having been separated out by sodium carbonate, the alkaline liquid, which after concentration *in vacuo* appeared in the form of a saponaceous mass (36 g from 35 g menthone), was acidulated and extracted with ether. From the ethereal extract a small quantity of liquid with an acid reaction could be isolated with steam (2 l. of distillate required 1,9 g. sodium carbonate for neutralisation), and in this formic acid was detected. The principal part volatilised very sparingly with water vapour and yielded 13,8 g. of an acid which, when reconstituted from the silver salt, boiled between 173 and 177° (12 mm.). The analyses of the silver salt and of the oxime (m. p. 99 to 100° from water)

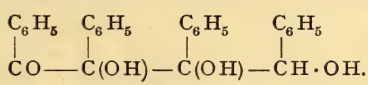
[1]) Liebig's Annalen **296** (1897), 131.

[2]) Berl. Berichte **34** (1901), 2984; **42** (1909), 145; Report April **1909**, 138.

gave for the acid the formula $C_{10}H_{18}O_3$. It consisted of keto-menthylic acid, which had already been obtained by Arth as well as by Beckmann and Mehrländer[1]) by oxidation of menthol. In the auto-oxidation of menthol, therefore, the ring opens, as shown in the subjoined formulæ:



Further additions to the knowledge of the chemical action of light have been made by Ciamician and Silber[2]) in the course of investigations into the effect of light upon benzaldehyde. They discovered that after exposing benzaldehyde to light from March 19th 1905 to October 30th 1907, there had formed in it a small quantity of white crystals, insoluble in ether, which, when recrystallised from glacial acetic acid melted at 245 to 246° and which, upon analysis, proved to be identical with the trimeride of benzaldehyde $(C_7H_6O)_3$, which had already been described by Mascarelli[3]). From the portion which was soluble in ether there were isolated benzaldehyde, benzoic acid and hydrobenzoin (m. p. 136°) as well as a resin which, when purified by dissolving it in ether, and precipitated with petroleum ether, appeared in the form of a white powder, m. p. 160 to 170°. By determining its molecular weight, in the supposition that it was a polymeric benzaldehyde, its formula $(C_7H_6O)_4$ was traced, and proved by the preparation of the semicarbazone melting at 232°. This, upon analysis, gave the figures for a mono-semicarbazone of the tetrameric aldehyde. The authors surmise this tetrameride to be a body constituted as follows: —



Ciamician and Silber also report on the action of light upon safrol and *iso*-safrol, as well as upon methyl-eugenol and methyl *iso*-eugenol in the presence of iodine.

Safrol and *iso*-safrol were exposed to light for a year, a trace of iodine being added to them. At the end of that period the safrol was found unchanged, while the *iso*-safrol had been converted into a brown mass of resin, interspersed with crystals of di-*iso*-safrol (m. p. 145 to 146°, from alcohol). Methyl-eugenol and methyl *iso*-eugenol showed similar differences in their behaviour, the former having undergone no change in a year, while the latter had become converted into a mass

[1]) Liebig's Annalen **289** (1896), 369.
[2]) Berl. Berichte **42** (1909), 1386.
[3]) Gazz. chim. ital. **36**, II. (1906), 670.

of resin, from which was isolated a white body crystallising in small needles, m. p. 96° (from methyl alcohol) and possessing the constitution of di-methyl *iso*-eugenol. This body, however, does not appear to be identical with the dimethyl *iso*-eugenol, m. p. 106°, which has been described by Széki[1]) and by Francesconi and Puxeddu[2]). These examples show once more that the propenyl-group is more readily affected than the allyl-group and also more readily shows symptoms of polymerism.

Benrath's experiments[3]) have shown that benzaldehyde, when affected by light, adds itself to many bodies. The authors therefore made experiments with benzaldehyde and safrol and *iso*-safrol. These showed that after a year's exposure to light the two isomerides had yielded the same additive product. The safrol had changed into a resinous mass which, after repeated boiling with alcohol, assumed the form of a sparingly soluble powder, m. p. 150 to 180°. The analysis agreed with $C_{17}H_{16}O_3$ (= $C_7H_6O + C_{10}H_{10}O_2$). The resinous mass which had been formed from the *iso*-safrol, when purified from methyl alcohol melted between 170 and 180°. Its analysis also agreed with the formula of the additive product $C_{17}H_{16}O_3$.

In 1891 G. de Varda[4]) published a paper in which he described a body which he had obtained from anethol by the action of the sun's rays. This body, which was regarded by de Varda as a polymeride of anethol, was called by him "photo-anethol". Recently P. Hoering and K. P. Grälert[5]) have succeeded in showing that de Varda's photo-anethol is not a polymeride of anethol, but di-p-methoxy stilbene. The authors repeated de Varda's experiments by exposing anethol (b. p. 113,5° at 14 mm.) for 10 months in sealed glasses to the influence of sunlight. At the close of the experiment the anethol had become yellow, and boiled at 108 to 111° (13 mm.) leaving a slight proportion of a viscous residue from which a crystalline body was obtained which, when purified with ether and recrystallised from benzene, melted at 208 to 210°. The yield was 0,18 g. from 200 g. anethol. The alcohol which had been distilled off was again exposed to light, and again yielded 0,42 g. of the same crystalline body. This substance, the photo-anethol of de Varda, is sparingly soluble in most solvents. Recrystallised from hot benzene or glacial acetic acid it forms brilliant small flaky crystals, melting between 214 and 215° (corr.) and showing a blue fluorescence, both in the solid

[1]) Berl. Berichte **39** (1906), 2422.
[2]) Gazz. chim. ital. **39**, I. (1909), 202.
[3]) Journ. f. prakt. Chem. II. **78** (1906), 383.
[4]) Gazz. chim. ital. **21** (1891), 183.
[5]) Berl. Berichte **42** (1909), 1204.

state and in solution. Combustion, the determination of the molecular weight, as well as comparison with the body prepared synthetically by Fritsch' and Wiechell's method[1]), showed that "photo-anethol" is really di-p-methoxy stilbene.

For purposes of further identification, the dibromide compound, a body which crystallises out from benzene in short needles (m. p. 178°), was prepared. The authors are of opinion that it is probable that di-p-methoxy stilbene is formed from anisic aldehyde, which is well known to form readily from anethol when it is left exposed to light and air[2]).

Pharmaco-physiological Notes.

A few years ago we reported upon a paper by R. Kobert[3]) on the therapeutic value of essential oils. The same subject is treated by L. Mazuyer[4]) in an article which contains nothing novel, and of which it is therefore sufficient merely to record the appearance.

L. Lutz and G. Oudin[5]) have examined crystallised apiol, oil of parsley, French, Austrian and German apiolin (?), myristicin, yellow and green liquid apiol (?), and the products of the fractionated distillation of oil of parsley, of French apiolin and of the green liquid apiol for their physiological action. They arrived at the following conclusions: The toxicity of the constituents of parsley seed is greater in the case of intra-peritoneal than in that of intra-muscular injection. It stands in proportion to the volatility of the products. The therapeutical action of liquid apiol (?) cannot be ascribed merely to the presence of crystalline apiol. The paper further discusses the anti-spasmodic and emmenagogue action which belongs to all constituents of parsley, with the exception of myristicin.

As a counterpart to Rosenthaler's work[6]) on asymmetric decomposition by enzymes which was mentioned in our last Report, we may here refer to a recently published article by P. Mayer[7]) on asymmetric syntheses. Mayer deals with the separation of l-campherol (*i. e.* camphor combining with glycuronic acid) after internal administration of i-camphor to dogs. We have already mentioned[8]) that in the animal organism

[1]) Liebig's Annalen **279** (1894), 341.
[2]) Comp. Report October **1904**, 42.
[3]) Report October **1903**, 109.
[4]) Journ. de la Parfumerie et Savonnerie **22** (1909), 74.
[5]) Bull. d. Sciences Pharmacol. **16** (1909), 68. From Chem. Zentralbl. **1909**, I. 1254.
[6]) Biochemische Zeitschrift **1908**, 238; Report April **1909**, 17.
[7]) Biochemische Zeitschrift **1908**, 439. From a copy kindly sent to us.
[8]) Report April **1902**, 83.

the camphor combines with glucuronic acid and hydroxylises in the course of the process. It appears from the results of Mayer's experiments in the administration of inactive camphor to dogs that formation of an asymmetric glycuronic acid compound may take place in the organism. Mayer observed that after giving dogs i-camphor (5 g. daily for 10 days) with their food, the urine became lævorotatory (corresponding to a glucose content of 1,6 %). By itself this lævorotation signifies nothing, for the camphor separates out as d- and l-camphor-glucuronic acid (?camphorol-glucuronic acid) which do not constitute optical antipodes. In order to determine whether this camphorol itself was optically active, it was isolated by splitting-up the acid (boiling with 10 per cent. sulphuric acid) and, after having been identified by the semicarbazide-compound (m. p. 232 to 234°) its optical behaviour was examined. The specific rotation in absolute alcohol was found to be $[\alpha]_{D17^\circ} - 5{,}91^\circ$; while that of pure l-camphorol, as observed by Magnus-Levy was $[\alpha]_D - 32{,}93^\circ$. Hence the camphorol formed within the organism from i-camphor consisted to the extent of 17,9 % of the lævo-rotatory variety, from which it was further to be concluded that the two optically active isomerides of camphor are not converted in the organism in the same degree. The investigations by Langgaard and Maass[1]), Hämäläinen[2]), and Bruni[3]), to which we have already referred, prove that their pharmacological action also differs.

On the action of citronella-grass on the tsetse-fly (*Glossina palpalis*), see p. 44.

On the physiological action of cypress oil, see p. 53.

On cases of poisoning with methyl salicylate, see p. 128.

On the alleged toxicity of vanillin, see p. 143.

Phyto-physiological Notes.

M. Mirande[4]) has recently reported on a peculiar occurrence observed by him in the case of plants containing glucosides. By exposing plants containing amygdalin to the action of mercury vapours, or carbon disulphide, or of anæsthetics, such as chloroform, he found that hydrocyanic acid was liberated. According to a communication by L. Guignard[5]) the cruciferous plants containing sinigrin, such as mustard and horseradish, liberate oil of mustard under similar conditions, while *Gaultheria procumbens* yields methyl salicylate.

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[1]) Therap. Monatsh. **20** (1907), 573; Report April **1908**, 176.
[2]) Skandinav. Archiv f. Physiologie **21** (1908), 64; Report April **1909**, 113.
[3]) Gazz. chim. ital. II. **38** (1908), 1; Report April **1909**, 161.
[4]) Compt. rend. **149** (1909), 140.
[5]) Compt. rend. **149** (1909), 91.

Hydrocarbons.

α-Pinene. It might be assumed that by eliminating water and carbon dioxide gas from nopinol-acetic acid it would be just as feasible to obtain *α*-pinene as *β*-pinene. Up to the present, however, Wallach[1]) had only succeeded in carrying out the synthesis of *β*-pinene, but now, by the application of special experimental conditions, this investigator has also been able to obtain lævo-rotatory *α*-pinene[2]). 120 g. nopinol acetic acid, m. p. 84 to 85°, were subjected to slow distillation by a hydrogen current in portions of 30 g. each, the receivers being changed whenever the temperature of the vapour emitted exceeded 165°. The resultant hydrocarbon was then fractionated over sodium. All fractions gave on all oxidation by means of 1 per cent. permanganate, nopinic acid, (m. p. 126 to 127°), as well as *β*-pinene glycol and a keto-acid, m. p. 68 to 99°, ($[\alpha]_D$ — 93,2° in a 7,16 per cent. chloroform solution; semicarbazone, m. p. 205°; oxime, m. p. 127 to 128°). This acid proved to be identical with the l-pinonic acid prepared by Gildemeister and Köhler[3]) as well as by Barbier and Grignard[4]). Mixed with equal parts of d-pinonic acid it also yielded the well-known inactive pinonic-acid, m. p. 103 to 104°. This proves that, besides *β*-pinene, l-*α*-pinene is also formed from nopinol acetic acid. Attempts to separate the *α*-pinene in the form of the nitroso-chloride were unsuccessful. In this case also, it was shown that in the case of pinene-fractions of high activity the absence of the nitroso-chloride reaction is no proof of the absence of *α*-pinene[5]).

The research as to the oxidation of active pinene into the active pinonic acids, which has been stimulated by the occurrence of l-pinocamphone in oil of hyssop[6]), has led us to endeavour to elucidate the hitherto unsolved questions why the yield of nitroso-chloride from pinene-fractions of high activity is so small, and why the crystallised pinene nitrosochloride has hitherto been obtained in an inactive form only[7]). These questions are of high importance, especially in the examination of turpentine oils and of essential oils which have been adulterated with turpentine.

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[1]) Liebig's Annalen **363** (1908) 9; Report November **1908**, 172.

[2]) Liebig's Annalen **368** (1909), 1.

[3]) Wallach Jubilee-publ. 1909; Report April **1908**, 59; April **1909**, 120.

[4]) Compt. rend. **147** (1908), 597; Report April **1909**, 120.

[5]) Comp. Gildemeister and Köhler, Wallach Jubilee public. 1909; also see below.

[6]) Comp. Report April **1908**, 58; April **1909**, 120; also compare below, and p. 68 of the present Report.

[7]) This investigation forms part of E. Gildemeister's and H. Köhler's contribution to the Wallach Jub. publication, p. 414: Über das Vorkommen von *β*-Pinen und l-Pinocamphon im Ysopöl und einige Beobachtungen über Isomerien in der Pinenreihe. (Vandenhoek & Ruprecht, Göttingen, 1909).

Both Kremers and Tilden[1]) had already observed that the yield of solid nitroso-chloride decreases with the increase in optical activity of the raw material used. We believe that this fact has its foundation in the different degrees of inclination to crystallise of the active and the inactive variety. Several experiments with pinene of different rotation, all carried out in the usual manner under conditions as far as possible similar, clearly showed the dependence of the nitroso-chloride yield upon the degree of rotation of the material employed. While 100 g. of inactive pinene yielded 30 g. nitroso-chloride, 100 g. of pinene with a specific rotation $[\alpha]_D + 46{,}73°$ only produced 3,6 g. of inactive pinene nitroso-chloride. But for practical work corresponding allowances must be made as regards the pinene determination, for in certain circumstances the detection of adulterations of essential oil with pinene by the aid of the nitroso-chloride may be impossible if the pinene has a high rotatory power. In such cases oxidation into the active pinonic acid, although less convenient, may give more certain results[2]).

It therefore became a matter of great interest to find a pure, optically active pinene, in order that its rotatory power and its behaviour towards nitrosyl-chloride might be examined. The way to the synthesis of an active pinene had been shown by Tchugaeff's experiments[3]), for that investigator had obtained the racemic compound from i-pinocampheol by his xanthogenate-method. It was therefore to be expected that from the l-pinocampheol which we had obtained from l-pinocamphone we might derive a pure active pinene. The preparation which was obtained had a pinene-odour and possessed the following constants: b. p. 156° (759 mm.), $d_{15°}$ 0,8644, $\alpha_D + 11° 5'$, $n_{D15°}$ 1,46793, $n_{D20°}$ 1,46625, mol. refr. found 43,78, calc. for a hydrocarbon $C_{10}H_{16}$ 43,54. Although these constants are in agreement with those of pinene, the unexpectedly low rotation caused some surprise. It was found, in fact, that only a small part of the hydrocarbon consisted of active pinene. Not a trace of nitroso-chloride could be obtained from 10 g. When oxidised with permanganate we obtained, besides a little active pinonic acid (m. p. 65°), an acid $C_{10}H_{16}O_4$, probably an isomeride of camphoric acid. It was impossible to determine from which hydrocarbon the latter acid was derived.

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[1]) Report October **1904**, 110.

[2]) In the meantime an article by Wallach has appeared on the same subject (Liebig's Annalen **368** (1906) 6, compare this Report, p. 165). Wallach obtained a similar result in the case of the examination of a synthetically prepared highly active pinene.

[3]) Journ. Russ. phys.-chem. Ges. **39** (1907), 1324. Through Chem. Zentralbl. **1908**, I. 1179; Report November **1908**, 171.

Barbier and Grignard[1]) have continued their investigations into the hydration of pinene. The process already described[2]) was modified to this extent that to 1 kilo of pinene from French oil of turpentine (b. p. 155 to 160°) there were added 1 kilo of glacial acetic acid, 100 cc. of a 50% benzene-sulphonic acid, and 100 cc. acetic acid anhydride. After mixing the temperature rises to 70°. Instead of leaving the mass to stand for 12 hours, as in the older process, it was worked up after $1^1/_2$ hours. The subsequent treatment is the same. The hydrocarbons were separated from the esters by fractionation. The same reaction was continued each time with the recovered hydrocarbon until no further hydration took place. This point was reached after five or six repetitions.

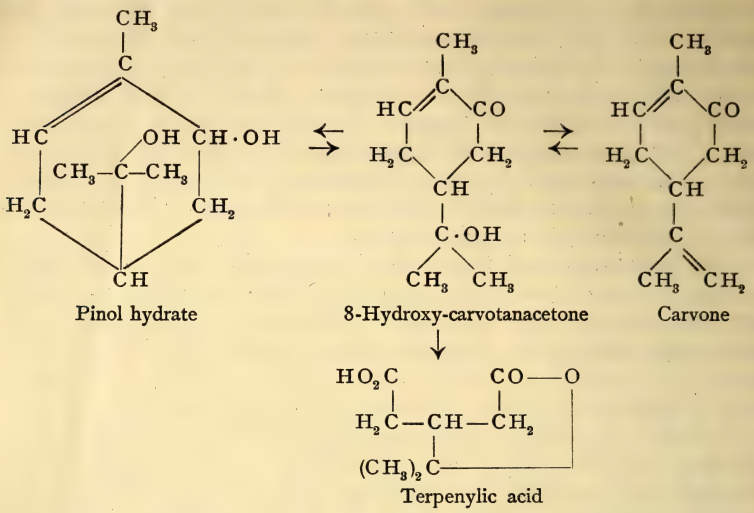
The examination of the products of reaction was carried out separately. It was shown that β-pinene (nopinene) was first attacked and converted into fenchyl alcohol. β-pinene therefore, appears to be the starting-point in the formation of fenchyl alcohol. This hydration renders an analysis of French turpentine oil possible. The pinene which remains behind after elimination of the β-pinene is much purer.

α-Pinene is chiefly converted into α-terpineol in the course of the hydration process referred to. In addition to it small quantities of terpadiene are formed, but these will also disappear as soon as it becomes possible still further to reduce the temperature. The hydrocarbons which hydratise less readily consist of a hydrocarbon which when impure boils at 150 to 152°, a camphene (m. p. 42°) which is converted by the hydration into borneol and *iso*borneol, and a liquid saturated hydrocarbon $C_{10}H_{18}$ (b. p. 157 to 160°).

As we have already mentioned[3]) Balbiano and Paolini, when oxidising pinene with mercuric acetate, obtained a ketone-alcohol $C_{10}H_{16}O_2$, which they afterwards[4]) described as Δ^6-6-hydroxymenthenone-2. But from a recent paper by G. G. Henderson and J. W. Agnew[5]) it appears that this alcohol is not Δ^6-**6**-hydroxymenthenone-2 but Δ^6-**8**-hydroxymenthenone-2. The formation of this body proceeds as follows: First, i-pinol hydrate is formed from the pinene and from this, by further oxidation a hydroxyketone, m. p. 154° (10 mm.). By acting upon this ketone with anhydrous oxalic acid there results a mixture of carvone and carvacrol; reduction with sodium in moist etherial solution regenerates pinolhydrate; reduction with hydriodic acid at ordinary temperature yields carvacrol; oxidation with permanganate of potassium,

[1]) Bull. Soc. Chim. IV. **5** (1909), 512, 519.
[2]) Comp. Report April **1908**, 178.
[3]) Berl. Berichte **35** (1902), 2995; Report April **1903**, 83.
[4]) Berl. Berichte **36** (1903), 3575; Report April **1904**, 100.
[5]) Journ. chem. Soc. **95** (1909), 289.

terpenylic acid. These reactions show the body to be an 8-hydroxy-carvotanacetone (Δ^6-8-hydroxymenthenone-2), which had already been prepared previously by Rupe and Schlochoff[1]).



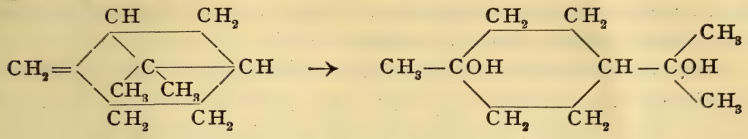
β-Pinene. According to Wallach[2]) the preparation of β-pinene free from α-pinene is carried out by distilling nopinol-acetic acid with acetic anhydride. In this process there remains in the residue an acid $C_{13}H_{22}O_5$ (m. p. 58 to 59°) which crystallises out in needles. This acid, of which the gross composition agrees with $C_{11}H_{18}O_3$ (nopinol acetic acid) + $C_2H_4O_2$ (acetic acid) was split up, by heating for two hours with caustic soda liquor, into acetic acid and an isomeric nopinol-acetic acid, m. p. 85 to 86°. The latter acid is also differentiated from nopinol-acetic acid by the fact that when distilled in a hydrogen current it only yields very few volatile products of decomposition. Wallach declines to attempt an explanation of this interesting process of isomerism until further experimental facts are available.

As it is, therefore, now possible, by treating nopinol-acetic acid with acetic anhydride, to obtain an α-pinene free from β-pinene, Wallach has also examined a few conversions of this hydrocarbon which had not been more closely investigated up to the present.

By shaking β-pinene with 3% sulphuric acid for several days a small quantity of terpin hydrate is obtained, the larger part, however, being converted into a hydrocarbon boiling between 170 and 175°. But if, on the other hand, β-pinene is left to stand for some time

[1]) Berl. Berichte **38** (1905), 1719; Report October **1905**, 112.
[2]) Liebig's Annalen **368** (1909), 6.

in alcoholic solution with nitric acid (d 1,255), an ample yield of terpine hydrat, m. p. 116 to 117°, is obtained.



β-Pinene Terpin-hydrate

Wallach had already on a previous occasion, while oxidising β-pinene, obtained pinene-glycol[1]), m. p. 75 to 77°. If this glycol really possesses the constitution attributed to it, it ought to be converted into nopinic acid upon oxidation. As a matter of fact this acid (m. p. 126 to 127°) was obtained by carrying out the process of oxidation by means of 1 per cent. solution of permanganate with the addition of a few drops of caustic soda liquor, at 0°. If on the other hand the glycol be oxidised at 50°, no nopinic acid, but another acid which has not been more closely investigated, is obtained.

Isopinene, Pinolene. In an earlier Report we stated that Aschan[2]) by decomposing the mixture of liquid chlorides eliminated in the process of preparing pinene hydrochloride with bases, had isolated a hydrocarbon which he called pinolene. From pinolene hydrochloride he obtained by treatment with aniline an isomeric terpene to which he gave the name of isopinene. In a new article, which deals with both terpenes, Aschan[3]) publishes the constitution of isopinene, which he has ascertained with some certainty. He further discovered pinolene to be a mixture of two hydrocarbons which he calls α- and β-pinolene. By oxidising by means of permanganate of potassium at 60 to 80° the two were separated, the α-pinolene being completely destroyed, while β-pinolene was not attacked. When quite pure, β-pinolene appears as a liquid possessing the following constants: b. p. 142 to 144°, $d_{4°}^{20°}$ 0,8588, α_D + 0,24°, $[\alpha]_D$ + 0,28°, $n_{D20°}$ 1,44769, mol. refr. found 42,37, calc. 41,83 for a tri-cyclic saturated hydrocarbon, or 43,53 for a hydrocarbon with one ethylene-bond.

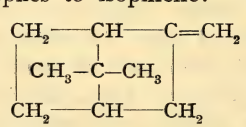
From β-pinolene Aschan obtained, without recrystallisation, a hydrochloride melting at 25 to 26° which does not appear to be identical with that previously prepared from pinolene[4]), although, when treated with anilin it also yields isopinene. The acid (m. p. 200°) which has previously been detected when oxidising pinolene with permanganate

[1]) Liebigs Annalen **363** (1908), 1; Report November **1908**, 172.
[2]) Berl. Berichte **40** (1907), 2250; Report October **1907**, 136.
[3]) Ofversigt af Finska Vetenskaps-Societetens Förhandlingar **51**, 1. Afd. A, Nr. 9. From a copy kindly sent to us.
[4]) Report October **1907**, 136.

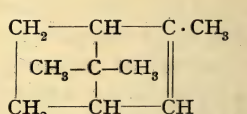
of potassium has now been investigated more closely. It is formed by oxidising α-pinolene, and by analysis and the determination of bases it was identified as racemic camphoric acid. Regenerated from the anhydride, the acid melts at 202°

Pure isopinene has the following constants: b. p. 154,5 to 155,5°, $d_{4°}^{20°}$ 0,8658, α_D + 2,61°, n_D 1,470253, mol. refr. calc. 43,53, found 43,48. After heating for 8 hours with permanganate of potassium in 1,5 per cent. aqueous solution at 60 to 70°, the constants of the unattacked isopinene had remained almost unchanged. In the process of oxidation two acids were obtained, the first (A), crystallising from water in small, thickish flakes or prisms, m. p. 126 to 128°; the other (B), easily soluble in water and melting at 200°. Acid A had the formula $C_{10}H_{16}O_3$; it is a keto-acid, as is shown by the phenyl hydrazone (although this is unstable), and the semicarbazone. Acid B was identified as *cis*-apocamphoric acid by its constitution ($C_9H_{14}O_4$), its inactivity and the forming of an anhydride melting at 178 to 179°. From these facts, Aschan concludes that only one of the formulæ I and II applies to isopinene: —

I.

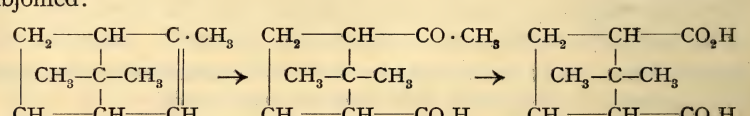


II.



The first of these has been considered by Wallach for D-l-fenchene or L-d-fenchene. As fenchene, when oxidised, yields hydroxy fenchenic acid (m. p. 153°) it follows that formula I. cannot apply to isopinene.

The keto-acid, m. p. 126 to 128° (called fenchenonic acid by Aschan), gives, when oxidised with bromine and alkali, apocamphoric acid. Hence the oxidation of isopinene proceeds in the manner subjoined:

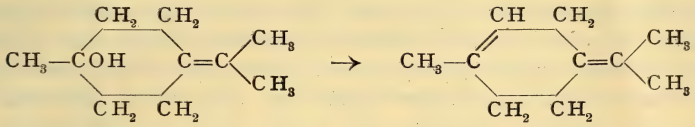


Isopinene — Fenchenonic acid — Apocamphoric acid

Limonene. On the use of limonene in the preservation of phosphorated oil, see Orange oil, p. 66.

Terpinolene. Oxidation of terpinene obtained by the customary methods yielded as its principal product α, α′-dihydroxymethyl-*iso*propyl-adipic acid, and the erythritol $C_{10}H_{16}(OH)_4$ m. p. 237°. The acid is no doubt formed from α-terpinene ($\Delta_{1,3}$-dihydrocymene), while the erythritol most probably is derived from γ-terpinene ($\Delta_{1,4}$-dihydrocymene).

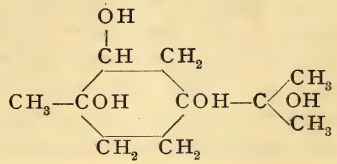
As terpinene may very easily be found in conjunction with terpinolene, it was necessary to oxidise terpinolene under the same conditions. Wallach[1]) by his previous investigations, had already shown that the erythritol could not be obtained from the ordinary terpinolene, but owing to the importance of the question he regarded it as necessary, with this end in view, once more to examine a terpinolene of the greatest possible purity[2]). As the methods hitherto employed for preparing terpinolene did not yield a sufficiently uniform product, Wallach employed γ-terpineol for preparing terpinolene, and converted the former into the latter body by splitting-off water with anhydrous formic acid:



γ-Terpineol Terpinolene

The hydrocarbon thus obtained boiled at 181 to 185° and gave a plentiful yield of terpinolene tetrabromide, m. p. 116°. With nitrous acid it gave no reaction for α-terpinene.

The hydrocarbon was oxidised in the familiar manner. No trace was obtained of the erythritol melting at 237°, but an isomeric erythritol was isolated. The compound crystallises with water of crystallisation; it begins to fuse at as low a temperature as 90° and melts over 100° irregularly with liberation of gas (up to about 130°). This erythritol of terpinolene (see formula above) is therefore entirely different from that obtained from crude terpinene. When further oxidised with permanganate it of course produced no α, α'-dihydroxymethyl*iso*propyladipic acid.



Terpinene. Several investigators have lately again turned their attention to the composition of terpinene. Semmler[3]) has published an article dealing with the inversion-products of carvenene. The isocarvenene which was obtained from carvenene by the action of alcoholic sulphuric acid proved to contain a high proportion of terpinolene, for when treated with bromine 3 g. *iso*-carvenene gave 0,5 g. tetrabromide, m. p. 116 to 117°. This m. p. was not lowered in mixture with terpinolene tetrabromide. It would thus appear that the inversion tends towards terpinolene in a not inconsiderable measure.

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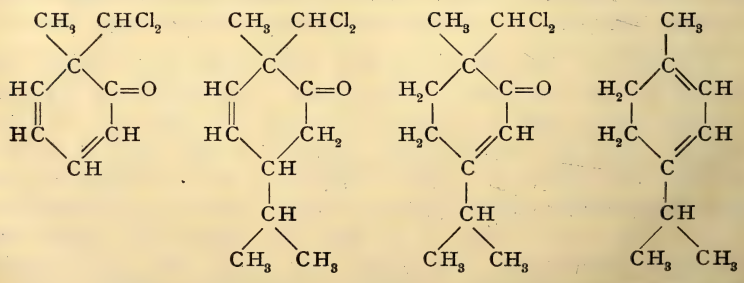
[1]) Liebig's Annalen **362** (1908), 285; Report November **1908**, 174.
[2]) Liebig's Annalen **368** (1909), 10.
[3]) Berl. Berichte **42** (1909), 522; Report April **1909**, 122.

Kondakow[1]), who lays special stress upon the extent to which his investigations have contributed to throw light upon the constitution of the terpinene-derivatives, concludes from the methods of preparing terpinene, as well as from its leading physical and chemical properties, that the hydrocarbon which formed the crystalline nitrosite, m. p. 155°, is a $\Delta^{1,4}$-menthadiene. It would lead us too far to reproduce Kondakow's views, which are not supported by experimental facts, and we therefore refer to the original paper.

The author obtained a hydrocarbon of the probable constitution of $\Delta^{1,3}$-menthadiene by splitting off 2 molecules of hydrochloric acid from the dichloride of the secondary-secondary diolalcohol, by means of alcoholic potash: b.p. 178 to 181°, $d_{20°}$ 0,846. This body is optically inactive and gives no solid di-haloid anhydrides. Kondakow has succeeded in reducing the dimethyl thymo-hydroquinone by Sabatier's and Senderens' method and hopes in this way to arrive at terpinene.

We are indebted to Auwers for a most interesting contribution on the solution of the terpinene problem. This author has continued with F. von der Heyden[2]) the researches on the synthesis of hydroaromatic hydrocarbons, which he had begun in collaboration with M. Hessenland. As his raw material he employed methyl-dichloromethyl-keto-dihydrobenzene (I), prepared from o-cresol by the action of chloroform and alkali. This body was converted into the higher homologues of methyl-dichloro-methyl-keto-dihydrobenzene by acting upon it with magnesium alkyl-iodide (II). By means of concentrated sulphuric acid the resultant product was converted into the isomeride (III), and by boiling with alcoholised potash he obtained the corresponding hydrocarbon (IV). By using magnesium isopropyl iodide he obtained $\Delta^{1,3}$-menthadiene (α-terpinene).

I. II. III. IV.



Decomposition by means of oxidation, and the preparation of the nitrosite (m. p. 155°) afforded proof that the body in question was

[1]) Journ. f. prakt. Chem. II. **79** (1909), 497.
[2]) Berl. Berichte **42** (1909), 2404.

in reality α-terpinene. It is difficult to say, of course, to what degree this body is pure, for no means of testing this are available.

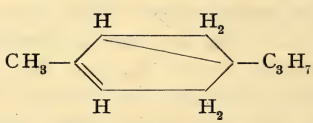
The optical examination of $\Delta^{1,3}$-menthadiene and of the lower homologues prepared by Auwers and von der Heyden made it possible to make most interesting comparisons as to the extent to which a hydrocarbon changes its properties by the passing over of a remote double-linking of the ring into a conjugated double-linking The optical examination of the homologous ketones already showed that when a double-linking of the ring assumes a conjugated position to the double-linking of the carbonyl, an increase of b. p., density, refraction, and dispersion may be observed. In the case of the hydrocarbons the same conditions became clearly apparent, affording new and conclusive proof that conjugated hydrocarbon double-linkings in a hexacyclic ring produce the optical effect which is to be expected in accordance with Brühl's rule. In the case of these bodies the exaltation of the molecular refraction is for M_α and M_D on the average 0,81, which is quite in accord with other observations. The molecular dispersion is even increased by about 40% above the normal value.

These observations induced Auwers[1]) to go deeper into the terpinene question itself. There are about 18 different methods of preparing terpinene-products. Five of these may finally be derived from terpin and therefore belong together. They differ from the other preparations by their strikingly high sp. gr. and low index of refraction. In every case the molecular refraction falls below the value M_D 45,24 which has been calculated for the formula $C_{10}H_{16}/\overline{2}$. Four other preparations form a second correlated group, all of them having had their origin in the splitting-off of hydrohalogen from the terpinene mono- and dihydrohaloids. They are differentiated from the first group by a lower sp. gr. and a higher index of refraction, hence the molecular-refraction is considerably greater in the case of this group. Their average exaltation is 0,45. The other methods of preparation in which sabinene, sabina-ketone, dihydrocarveol, carvylamine, carvenone, and the chlorinated ketone are the primary substances, yield terpinenes of more or less especially high exaltation. This clearly shows the connection with the modes of preparation. In order to convert terpine into terpinene it is necessary to split off water twice, and conditions ensue which make the formation of tetra rings not improbable, but which in any case do not favour the formation of conjugated double linkings. The optical examination also agrees with this. In the case of the terpinene hydrohaloids the conditions are more favourable to the formation of a system of conjugated double-linkings. The high exaltation which is shown by the terpinene-preparation from dihydrocarveol warrants the conclusion

[1]) Berl. Berichte 42 (1909), 2424.

that this body in particular contains a larger proportion of Wallach's α-terpinene than of the γ-compound. The terpinenes which are obtained from phosphate of carvenylamine by dry distillation, from chlorinated ketone and from chloro-carvenene, behave in a similar manner.

In all these instances, therefore, the terpinene preparations show the optical behaviour which is to be expected on the basis of their probable constitution, and of Brühl's rules for the optical activity of conjugated double-linkings. The synthesis of terpinene from sabina-ketone apparently contradicts the above findings. Auwers, however, is of opinion that these contradistinctions are entirely cleared up if we assume that the hydrocarbon which is formed consists of 50 % each of either α-terpinene and of a hydrocarbon with the formula



or of mixture of α- and γ-terpinene and the hydrocarbon in question.

It results from these investigations that all the processes which lead *via* terpin produce terpinene-derivatives in which α-terpinene can not be regarded as the characteristic constituent. From the terpinene hydrohaloids, the α-terpinene-content cannot be expected to exceed 50 % in the most favourable case. For obtaining α-terpinene-preparations which, although not pure, are of a comparatively high percentage, Auwers regards the method from carvone *via* dihydrocarveol as the best, on account of its ease and cheapness. Semmler regards carvenene as a particularly pure α-terpinene, but Auwers cannot agree with this view, because by this process also, the action of nascent hydrochloric acid produces conditions which afford no guarantee of a uniform final product. The optical investigation of chloro-carvenene and of carvenene, which has been repeated by Auwers, showed some slight discrepancies with the results of Klages and of Semmler, but it agreed in respect of the divergencies such as have been observed in the case of numerous other bodies with conjugated double linkings. Carvenene does not appear to be identical with α-terpinene from o-cresol. The latter possesses the lowest b. p. and the least density of all terpinenes known. It also differs from the others in its behaviour towards the action of sulphuric acid.

These results lead Auwers to regard it as beyond question that optically the terpinenes are no exception to Brühl's rules, and that in determining their constitution, the physical, and especially the optical, behaviour should occupy an important place, together with the chemical tests.

In his researches intended to elucidate the constitution of terpinene, Wallach has shown that the terpinene obtained from terpinene-dihydrochloride, pinene and sabinene-hydrate, contains *α*-terpinene ($\Delta_{1,3}$-dihydrocymene) and *γ*-terpinene ($\Delta_{1,4}$-dihydrocymene)[1]). It was therefore a matter of interest for Wallach to investigate also the structure of terpinene of different origin[2]). One of the longest-known modes of formation is that from bihydro-carvylamine. Dry distillation of bihydro-carvylamine hydrochloride yielded a hydrocarbon boiling at 174 to 178°, which, when oxidised, only gave very little *α*, *α'*-dihydroxymethyl-*iso*-propyladipic acid, m. p. 189°, and only traces of the erythritol which melts at from 236 to 237°. The preparation contained, therefore, but little terpinene. When bihydro-carvylamine phosphate, which was first prepared by Harries, was distilled, the result was a product boiling principally between 176 and 179°. This consisted for the greater part of *α*-terpinene; for in the process of oxidation considerable proportions of *α*-*α'*-dihydroxymethyl-*iso*propyladipic acid, together with a little erythritol were obtained. In the preparation from the phosphate, therefore, a further-reaching displacement of the ethylene-bond in the bihydro-carvylamine has ensued than in the case of the dry hydrochloride.

It will probably also be difficult to obtain a uniform product by the method recommended by Semmler for the preparation of *α*-terpinene *i. e.*, by reduction of monochloro terpinene (chloro-carvenene). By allowing the calculated quantity of phosphorus pentachloride to act upon diluted carvenone at a low temperature oxygen and dichlorinated bodies may easily be formed, while an excess of phosphorus pentachloride or increased temperature may favour the formation of cymene derivatives. This view of Wallach was confirmed by the fact that Klages and Kraith on the one hand, and Semmler on the other make different statements as to the monochloroterpene which resulted from carvenone. Wallach's experiments show that even when the work is conducted with the utmost care, preparations with very different properties are obtained.

The carvenone which was used in the experiments was carefully purified from the semicarbazone and treated with phosphorus pentachloride in petroleumether solution according to Semmler's indications. But the monochloride was by no means so readily formed as was to be expected from Klages' and Kraith's statements. Wallach did in fact succeed in obtaining fractions with the properties of the mono-chloride described by Semmler and Klages, but ultimate analysis of the product of investigation gave unsatisfactory figures, so that it was to be in-

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[1]) Liebigs Annalen **362** (1908), 285; Report November **1908**, 174.
[2]) Liebigs Annalen **368** (1909), 13.

ferred that the substance consisted partly of oxygenated bodies, partly of chloro-cymene and partly of dichloride. The preparations which had been purified by steam distillation, when fractionated, were all found to contain oxygen, even when an excess of phosphorus pentachloride was used.

It is therefore probable that the product of conversion consists of a mixture of monochloride and dichloride, the latter being again converted into carvenone during the distillation. In every experiment some parts were obtained which were lighter than water and others which were heavier. These results were specially confirmed by the analysis of the fractions boiling between 95 at 100° at 10 mm. in each experiment. The sp. gr. of pure monochloro terpinene therefore does not appear to be much higher than 1. Proof that the monochloride which is formed by the method described belongs to the terpinene series was afforded by oxidation into α, α'-dihydroxymethyl-*iso*propyladipic acid, which acid was also obtained liberally from the hydrocarbon obtainable by the reduction of the chloride with sodium in alcoholic solution.

G. G. Henderson and W. Cameron have investigated the action of chromyl chloride on terpinene[1]). While in the reciprocal action between chromylchloride and pinene[2]), camphene, or limonene additive products are the first to be formed, which only yield ketone- or aldehyde-like bodies when treated further, there results from terpinene a brown oil, almost entirely volatile with steam, from which, with bisulphite, α-p-toluylpropylic aldehyde, $C_{10}H_{12}O$, (b. p. 222° at 760 mm.; $d\frac{20°}{20°}$ 0,984; n_D 1,51436; mol. refr. 45,3; semicarbazone, m. p. 155°) was isolated. After elimination of the aldehyde, p-toluyl-methyl ketone (b. p. 109° at 14 mm., m. p. of the semicarbazone 204 to 205°), cymene, and a ketone $C_9H_{12}O$ which was not definitely identified, were shown to be present. As α-p-toluyl-propyl aldehyde and p-toluyl-methyl-ketone are cymene derivatives, the authors assume that terpinene is first oxidised by chromyl chloride into cymene, and that from the latter the aldehyde and the ketone are formed. These observations also throw a new light upon the results of the authors' earlier investigations into the action of chromyl chloride on limonene[3]). For it was shown that the products then obtained are identical with α-p-toluyl propylic aldehyde and p-toluyl-methyl ketone, and as a result the formula $C_{10}H_{14}O$, which was given for the aldehyde at the time, must be replaced by $C_{10}H_{12}O$, with which the analytical values of the semicarbazone too agree better.

[1]) Journ. Chem. Soc. **95** (1909), 969.

[2]) Report April **1900**, 55; October **1903**, 85; April **1904**, 108, April **1908**, 180; November **1908**, 171.

[3]) Comp. Report April **1908**, 180.

Phellandrene. The conversion of phellandrene into dipentene which was observed years ago by Wallach[1]) has again been noted by Bacon[2]) when boiling the oily hydrochloride of α-phellandrene from oils of elemi (b. p. 62 to 63° [9 mm.]; $d\frac{30°}{4°}$ 0,8364; $n_{D30°}$ 1,4673; free from dipentene) with alcoholic potash liquor beneath a reflux-condenser. The terpene which was separated out from the mixture by the familiar method, when brominated in an amylalcoholic-ethereal solution, gave large quantities of dipentene tetrabromide, m. p. 124° (from acetic ester).

Caryophyllene. Deussen's[3]) paper on the compounds formed by oxidation of caryophellene with permanganate of potassium has induced C. W. Haarmann[4]) to publish the results of some experiments which he made as long ago as 1905. He also obtained from caryophyllene by oxidation with permanganate of potassium a neutral product, m. p. 120°, but, judging from the analysis, this was not a compound $C_{15}H_{22}O_4$ as surmised by Deussen, but a body $C_{14}H_{22}O_4$. This body was of a glycol-like charakter and possessed the following constants: m. p. 120°, b. p. 210° (10 mm). When left to stand with a methylalcoholic solution of hydroxylamine it yielded an oxime $C_{14}H_{23}O_4N$, m. p. 188,5° (from water), which indicated the probable presence of a keto-group. When treated with 1 % sulphuric acid under heat, the glycol yielded an oily compound $C_{14}H_{22}O_3$, boiling at 193° (20 mm.) but from this no derivatives were obtained. Oxidised with chromic acid in solution of acetic acid, the glycol produced a solid aldehyde, $C_{14}H_{20}O_4$, which, when recrystallised from acetone, melted at from 156 to 157° and gave a mono-hydrazone, m. p. 167°, with phenyl hydrazine acetate. Oxidation of the glycol with permanganate of potassium in chloroform solution at ordinary temperature yielded 45 % of an acid, m. p. 171°; but from this no keto-derivative could be prepared.

The course of the oxidation process therefore renders it probable that caryophyllene contains two methylene-groups, one of which can be oxidised into a methyl-ketone group CH_3CO; while the other can be oxidised into the normal glycol $C(OH)\cdot CH_2(OH)$ and subsequently into the aldehyde $C(OH)\cdot CHO$ and the acid $C(OH)\cdot CO_2H$.

Alcohols.

Heptyl Alcohols. As mentioned by us formerly, saturated aliphatic hydrocarbons and alcohols have been discovered, although not

[1]) Liebig's Annalen **239** (1887), 44.
[2]) Philippine Journ. of sc. **4** (1909), A, 110.
[3]) Berl. Berichte **42** (1909), 376, 680; Report April **1909**, 124.
[4]) Berl. Berichte **42** (1909), 1062.

very often, in essential oils, *e. g.* heptane in the oil of *Pinus Sabiniana* Dougl.[1]), and octyl alcohol in the various heracleum oils. We therefore take this opportunity of calling attention to certain synthetically prepared isomeric heptyl alcohols concerning which L. Henry[2]) has reported.

If magnesium amyl-bromide $CH_3 \cdot (CH_2)_3 \cdot CH_2 MgBr$ is allowed to act upon acetaldehyde, there is formed methyl-amyl-carbinol, $CH_3CHOH \cdot (CH_2)_4 \cdot CH_3$. This is a liquid of pungent odour, b. p. 156—157° (762 mm.), $d_{20°}$ 0,8193, n_D 1,42131. By heating it with iodine and phosphorus this alcohol yields heptane-2-iodide $CH_3 \cdot CHI \cdot (CH_2)_4 \cdot CH_3$; b. p. 100° at 40—50 mm., $d_{20°}$ 1,304, n_D 1,48262. By treating the iodide with alcoholic solution of potassium sulpho-hydrate the former body yields heptane-2-thiol $CH_3 \cdot CHSH \cdot (CH_2)_4 \cdot CH_3$, a liquid insoluble in water; b. p. 164—165° (765 mm.), $d_{20°}$ 0,8353, n_D 1,44596.

When magnesium methyl-bromide is treated with ethyl valerate tertiary dimethyl-butyl carbinol $(CH_3)_2C(OH)(CH_2)_3 \cdot CH_3$ is formed. This is a colourless liquid of a powerful odour, insoluble in water, with the following constants: b. p. 141 to 142°, d 0,8155, n_D 1,41592. With concentrated hydrochloric acid this alcohol gives 2-methyl-2-chlorohexane, $(CH_3)_2CCl \cdot (CH_2)_3 \cdot CH_3$, b. p. about 135°, with slight decomposition.

So far, no glucosides of the terpene-alcohols were known, but E. Fischer and K. Raske[3]), have now succeeded in preparing the glucosides of menthol and borneol. Their process consists in subjecting the alcohols to the action of aceto-bromoglucose in the presence of silver carbonate. For instance, to a solution of 6 g. aceto-bromoglucose and 20 g. menthol in 50 cc. of dry ether, there were added 6 g. freshly prepared silver carbonate which had been washed with alcohol and ether and dried in the desiccator. When he generation of carbon dioxide gas had subsided, this mixture was shaken mechanically for two days. When the ethereal solution was evaporated there remained as a residue a colourless syrup which was freed from menthol by steam. The residue (5 g. = 70% of the theoretical quantity) was a friable mass, consisting, as shown by analysis, of tetra-acetyl menthol-d-glucoside $C_{10}H_{19} \cdot O \cdot C_6H_7O_5(C_2H_3O)_4$. The glucoside, m. p. 130°, dissolves readily in ether, acetic ester, acetone, benzol, and chloroform; more sparingly in alcohol, very slightly in water, and is almost insoluble in petroleum ether.

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[1]) Report October **1906**, 64; April **1907**, 85; October **1907**, 76.

[2]) Bull. Acad. roy. Belgique, Classe des Sciences, **1908**, 957—63. According to Chem. Zentralbl. **1909**, I. 1854.

[3]) Berl. Berichte **42** (1909), 1465.

In order to split off the acetyl-groups, 4 g. of finely powdered glucoside were heated 5 to 6 hours with a solution of 16 g. hydrated baryta crystals in 240 cc. water and 75 cc. alcohol to 55 to 60°, with frequent stirring. The warm liquid was saturated with carbon dioxide, the barium carbonate filtered off and washed with alcohol. The filtrates, when evaporated, left in the vacuum a syrup studded with white crystals, which for further purification was boiled with alcohol. When the filtrate was evaporated a pale yellow, slowly congealing syrup remained behind. This was dissolved in hot water and evaporated *in vacuo*, when the menthol-d-glucoside separated out from it (2,4 g. = 87 % of the theoretical yield).

Analysis of the product, dried at 60° under 15 mm., showed that it contained 1 mol. water of crystallisation which was only completely driven off after heating *in vacuo* to 100°. The hydrous menthol-d-glucoside melts gradually at 77 to 79°, after mollifying first, and is sparingly soluble in water, readily in alcohol, more sparingly in benzene and almost insoluble in petroleum ether: $[\alpha]_{D20°}$ — 91,9 to 93,0° (in alcohol).

The glucoside is rather easily hydrolysable with emulsin. Thus, 0,3044 g. of the sample, which had been dissolved in 50 cc. and diluted with 0,15 g. emulsin, after being left standing for 20 hours in the incubator had yielded 88 % of the theoretically possible quantity of glucose.

Tetra-acetyl borneol-glucoside $C_{10}H_{17}O \cdot C_6H_7O_5(C_2H_3O)_4$, was formed in exactly the same manner. It forms fine needles (from alcohol) m. p. 119 to 120°. After saponification the d-borneol-d-glucoside $C_{10}H_{17}OC_6H_{11}O_5$ was obtained. This body crystallises from water in fairly large needles, m. p. 134 to 136°; $[\alpha]_{D20°}$ — 42,1 to — 42,2° (in alcohol). Emulsin does not act very readily upon the glucoside. After being left to stand for 3 days in the heating stove only 40 % had been hydrolised.

Gluco-vanillin (vanillin-d-glucoside), described by Tiemann[1]), was prepared by a similar process. By shaking a solution of 10 g. aceto-bromo glucose in 75 cc. ethylic ether with a solution of 7,4 g vanillin for 3 days in the calculated quantity of n-soda liquor, 6,9 g. of tetra-acetyl-gluco-vanillin were obtained. When recrystallised from dilute alcohol this body formed colourless, thin prisms, m. p. 143 to 144°. After saponification gluco-vanillin was obtained which crystallised with 2 mol. water of crystallisation, in the same manner as does the preparation obtained from coniferin: m. p. 188 to 189°, $[\alpha]_{D20°}$ —87,13° (in water); according to Tiemann $[\alpha]_D$ — 88,63°.

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[1]) Berl. Berichte **18** (1885), 1596.

Pinocampheol. For the generation of hydrocarbons from active l-pinocampheol, m. p. 67 to 68°, see p. 166.

Borneol. In our Report of April **1908**, p. 150, we referred to the mode in which l-borneol was prepared in Tonquin from *Blumea balsamifera* D. C. (N. O. Compositæ). This process has been suggested in several quarters as suitable for the preparation of synthetic camphor. Bacon[1]) states that the plant occurs profusely in many parts of the Philippines and that attempts have been made in order to obtain camphor therefrom. From the leaves 0,1 to 0,4 % of a yellow oil was distilled, which had a camphoraceous odour, consisted of almost pure l-borneol, and may value from 50 to 75 % of the price of camphor. The tree flourishes very luxuriantly and it is said that the leaves can be collected four times yearly. Experiments in Indo-China have shown that a yield of 50000 kilos of leaves can be obtained per hectare, from which from 50 to 200 kilos of borneol can be prepared. It remains to be seen whether, in view of the fact that labour is not cheap in the Philippines, the cultivation and distillation can be carried on there at a profit.

Fenchyl alcohol. Most investigators have obtained only liquid chlorides from fenchyl alcohol. Kondakow[2]) alone has succeeded in isolating from it a solid chloride, m. p. 92°, which is regarded by Wallach[3]) as an impure bornyl chloride. In a further article Kondakow[4]) now returns to the question of the haloid-combinations from fenchyl derivatives. He did not succeed in converting the chloride (m. p. 92°) into camphene, and he regards this as a further proof that this chloride is derived from fenchyl alcohol.

From l-fenchyl alcohol he has obtained several solid chlorides. One monochloride possessed the following constants: m. p. 22°, $d_{20°}$ 1,004, $[\alpha]_{D\,20°}$ — 8,89°, n_D 1,4802, mol. refr. found 48,84, calc. 48,88. With alcoholic potash liquor this chloride is converted into a fenchene (b. p. 155 to 160°; $d_{18,5°}$ 0,869; $[\alpha]_D$ — 29,49°; n_D 1,468802; mol. refr. 43,57) and into a mixture of liquid alcohols containing fenchyl alcohol or *iso*fenchyl alcohol. In addition a second monohydrochloride with a b. p. 10° higher was formed. The fenchene obtained from the latter possessed the following constants: b. p. 155 to 161°, $d_{17,5°}$ 0,868, $[\alpha]_D$ — 23,27°, n_D 1,468505, mol. refr. found 43,59, calc. for $C_{10}H_{16}$ / 43,53. Apparently, these chlorides

[1]) Philippine Journ. of sc. **4** (1909), A, 127.

[2]) Journ. f. prakt. Chem. II. **62** (1900), 11 and **68** (1903), 115; Report October **1903**, 96.

[3]) Liebig's Annalen **362** (1908), 171; Report November **1908**, 189.

[4]) Journ. f. prakt. Chem. II. **79** (1909), 271.

do not yet constitute a uniform compound, but contain admixtures which affect their behaviour more or less.

Besides the solid monohydrochlorides, Kondakow was able to isolate a solid dihydrochloride of which the m. p. was found 24 to 26° below that of the previously prepared body. With moist oxide of silver it was converted into a terpin of which the m. p. varied, according to the crystalline form in which it separated out, between 100 to 104° and between 98 to 99°, and into a body with an odour of terpineol. It was impossible to distinguish precisely whether this dihydrochloride was a derivative of dipentene, terpinene, or carvestrene, but Kondakow inclines to the view that it represents *cis*-carvestrene dihydrochloride and its derivatives. In that case the chloride with m. p. 52,5°, which was previously described, would be *trans*-carvestrene dihydrochloride.

The bromides of fenchyl alcohol were capable of being split up into two portions with different b. p. No monohydrobromide was formed, but two dihydrobromides, m. p. 89° and 58 to 59° (54 to 56° when purified by crystallisation) respectively. In the case of a previous experiment, Kondakow had obtained from D-l-fenchyl alcohol two bromides melting respectively at 64° and 32°, which, however, are probably mixtures of *cis*- and *trans*-isomerides. The new bromides likewise gave considerable depressions of the m. p., mixtures of the two melting respectively at 43 to 70° and at 50 to 53°.

The new dibromide melting at 89° is certainly identical with Wallach's[1]) dibromide from D-l-fenchene. It was not capable of being converted into a terpin by means of silver oxide, but instead there resulted an unsaturated body of ether-like odour (b. p. 212 to 217°; $d_{18°}$ 0,925; $\alpha_{D\,18°}$ — 36,76°; n_D 147459). As stated by Kondakow himself, it would be premature to indulge in speculations with regard to the constitution of this body, because no fresh experimental facts have come to light since Wallach made his researches.

In conclusion Kondakow reports, by way of correction, that he endorses Wallach's opinion that isofenchyl alcohol is a secondary alcohol. On the other hand, Kondakow assumes a tertiary alcohol as an intermediate product of hydration.

Homologous fenchyl alcohols. See p. 202.

Guajol. A. Gandurin[2]) publishes a correction of his previous article, to which we referred at the time[3]), wherein he wrongly attributed to Semmler a statement as to the character of guajol as secondary alcohol.

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[1]) Liebig's Annalen **362** (1908), 192; Report November **1908**, 189.
[2]) Berl. Berichte **42** (1909), 1429.
[3]) Berl. Berichte **41** (1908), 4359; Report April **1909**, 127.

Juniperol. H. Ramsay[1]) reports on crystals of the sesquiterpene alcohol juniperol, $C_{15}H_{24}O$, obtained from juniper bark (?) by distillation with steam. The alcohol (m. p. 107°; d 1,0116; insoluble in water) was isolated from the fraction of the oil boiling between 130 to 155° (8 mm. press.) and occurred in thick, optically inactive, triclinous tables. Crystallographic examination gave the following results: 0,7243 : 1 : 0,7574, $\alpha = 90° 14'$, $\beta = 103° 30'$, $\gamma = 90° 5'$.

Aldehydes.

It is well known that many constituents of essential oils give additive products with acids. With the exception of a few of the most familiar, such as the combinations of cineol with hydrobromic acid and phosphoric acid and cinnamic aldehyde with nitric acid, these bodies have so far been very little explored. In this connection an article by A. Shukoff and F. Kassatkin[2]) is interesting, inasmuch as it describes a series of combinations of aldehydes and ketones with acids. For instance, when camphor is introduced into anhydrous nitric acid under cooling (both bodies in equi-molecular quantities) there is formed a viscous mass, which congeals in long needles when cooled and liquifies when exposed to air. This mass has the formula $C_{10}H_{16}O \cdot HNO_3$; it melts at 24° and is readily soluble in the usual organic solvents. Solutions of camphor and nitric acid in petroleumether produce a compound $(C_{10}H_{16}O)_2\ HNO_3$, m. p. 2,2°. When equimolecular quantities of camphor and phosphoric acid are heated the result is a body $C_{10}H_{16}O \cdot H_3PO_4$, which occurs as a liquid, solidifying in large crystals with m. p. 29°. When hydriodic acid gas is introduced into a solution of camphor and petroleum ether, the compound $C_{10}H_{16}O \cdot HI$ is formed. This is a reddish-brown crystalline mass, m. p. 29 to 30°[3]) and sparingly soluble. The introduction of hydrochloric acid gas into powdered camphor yields a colourless, mobile liquid additive product, which decomposes when exposed to air. This body congeals into a solid mass (m. p. 4,2°) when cooled. In the same manner nitrous acid anhydride and camphor yield a liquid body which does not congeal even at — 35°.

The product of a combination from benzophenone and nitric acid, $C_6H_5 \cdot CO \cdot C_6H_5 \cdot HNO_3$ is also described. This is a readily congealing liquid which, when recrystallised from ether, melts at 39°. It is further stated that benzaldehyde with nitric acid yields a cristalline

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[1]) Zeitschr. f. Kristallogr. **46** (1909), 281; through Chem. Zentralbl. **1909**, I. 1656.

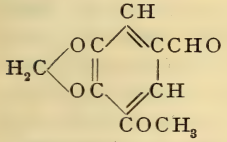
[2]) Journ. russ. phys.-chem. Ges. **41** (1909), 157. Through Chem. Zentralbl. **1909**, I. 1761.

[3]) Berl. Berichte **6** (1873), 936.

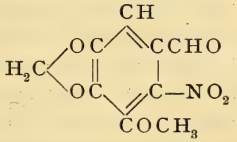
mass which cannot be easily purified. Judging by the melting-point curve this is a combination $C_6H_5 \cdot CHO \cdot HNO_3$, m. p. $+ 5{,}4^\circ$. (According to Germ. Patent 206 695, the m. p. lies at about -1°)[1]). Crystalline compounds were also obtained from œnanthol and from methylnonylketone.

It is known from the work of Thoms[2]) and his collaborators that nitric acid also acts in another manner by displacing aggregations of atoms,

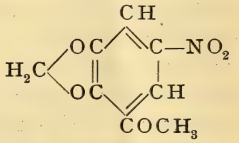
A similar process of reaction was observed by A. H. Salway[3]) in the course of the action of nitric acid upon myristicinic aldehyde. In this process, in addition to nitro-myristicinic aldehyde, there is formed, owing to substitution of the aldehyde groups, 5-nitro-1-methoxy-2, 3-methylenedioxybenzene, as shown by the following equations: —



Myristicinic aldehyde



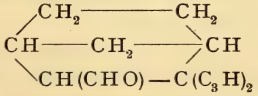
Nitromyristicinic aldehyde



5-Nitro-1-methoxy-2, 3-methylenedioxybenzene

It was clear from the analogous processes of acting with nitric acid upon anisic aldehyde, piperonal, and vanillin-methyl ether, that the reaction described above, viz., the displacement of the aldehyde-group by the nitro-group, applies generally to the ethers of the aromatic hydroxy-aldehydes. Accumulation of alkoxyl groups facilitates the substitution.

As Semmler[4]) has shown, aldehydes which have in adjacent positions one or more H-atoms of the CHO-group, when boiled with acetic acid anhydride and sodium acetate, give mono-esters, by reacting in the enolic form. By means of this reaction, Semmler[5]) was able to show that for camphenilanic aldehyde only the camphene formula applies, which contains a tertiary H-atom vicinal to the CHO-group.



Camphenilanic aldehyde

When camphenilanic aldehyde was boiled for an hour with acetic acid anhydride there was formed, in addition to a little di-acetate, enol-

[1]) Chem. Zentralbl. **1909**, I. 805.
[2]) Comp. Report October **1903**, 99.
[3]) Proceed. chem. Soc. **25** (1909), 160.
[4]) Berl. Berichte **42** (1909), 584; Report April **1909**, 128.
[5]) Berl. Berichte **42** (1909), 963.

camphenilanaldehyde monoacetate $C_9H_{14}:CH\cdot O\cdot OC\cdot CH_3$, with the following constants: b. p. 113 to 116° (10 mm), $d_{20°}$ 1,0125, n_D 1,4816, mol. refr. found 55,1, calc. f. ester $C_{12}H_{18}O_2$ / 54,61. Oxidation with ozone yielded camphenilone (b. p. 70 to 80°, 10 mm., $d_{20°}$ 0,970; n_D 1,471; m. p. of the semicarbazone 223°). Reduction with sodium in alcoholic solution gave the hitherto unknown camphenilyl alcohol $C_{10}H_{18}O$ (b. p. 105 to 106°, 10 mm.; m. p. 58 to 59°, not very clearly defined). This body belongs to camphenilanaldehyde. The corresponding chloride of the alcohol possessed the following constants: b. p. 83 to 85° (10 mm.), $d_{20°}$ 0,9909, n_D 1,4862. The oxidation as well as the reduction proved the unsaturated character of enol-camphenilanaldehyde acetate.

As two aliphatic aldehydes, oenanthic aldehyde and octylic aldehyde, when boiled with acetic acid anhydride, also react in the enolic form, Semmler[1]) regards it as probable that all aldehydes with CH_2-group vicinal to the CHO-group give this reaction. It is true that phenyl acetaldehyde (which had already been examined previously), also possesses a CH_2-group which is adjacent to the aldehyde-group, but it is not impossible that the phenyl-radical[2]) may have an "activating" influence upon the CH_2-group.

Oenanthic aldehyde (b. p. 42 to 43°, 10 mm.; $d_{20°}$ 0,8250; n_D 1,41655; m. p. of the semicarbazone 106 to 107° from methyl alcohol) yielded, besides the di-acetate, enol-n-heptanal monoacetate with the following constants: b. p. 76 to 79° (10 mm), $d_{20°}$ 0,888, n_D 1,43258, mol. refr. found 45,6 calc. for the ester $C_9H_{16}O_2$ / 45,0.

Octylic aldehyde supplied by us (b. p. 60 to 61°, 9 mm.; $d_{20°}$ 0,8211; n_D 1,41955; b. p. of the oxime 111 to 112°, 9 mm.; m. p. of the oxime 60°, from dilute alcohol; m. p. of the semicarbazone 101°) yielded enol-n-octanal-monoacetate $CH_3\cdot(CH_2)_5\cdot CH:CH\cdot O\cdot CH_3$, with the following constants: b. p. 90 to 94° (10 mm.), $d_{20°}$ 0,88, n_D 1,43256, mol. refr. found 50,1, calc. for the ester $C_{10}H_{18}O_2$ / 49,6. Only a little di-acetate had been formed in addition.

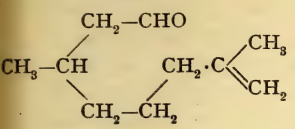
Aldehydes with a ramified chain also react in the enolic form when boiled with acetic anhydride[3]).

*Iso*valeric aldehyde (b. p. 92°, 760 mm.; $d_{20°}$ 0,8089; n_D 1,39488) gave enol-*iso*valeric aldehyde monoacetate, with the following constants: b. p. 127 to 133° (760 mm.), $d_{20°}$ 0,8818, n_D 1,41655. Here also diacetate was formed in addition.

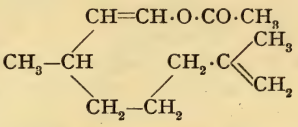
Citronellal (b. p. 83,5 to 87,5° [10 mm.]; $d_{20°}$ 0,8627; $[\alpha]_D$ +10°; n_D 1,45262) likewise gave, together with diacetate, enol-citronellal monoacetate (b. p. 110 to 115° [10 mm.]; $d_{20°}$ 0,900; $[\alpha]_D$ —1°;

[1]) Berl. Berichte **42** (1909), 1161.
[2]) Berl. Berichte **42** (1909), 584; Report April **1909**, 128.
[3]) Berl. Berichte **42** (1909), 2014.

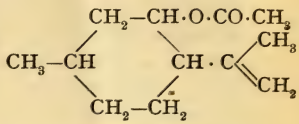
n_D 1,45762). When boiled for 20 hours with acetic anhydride and a trace of glacial acetic acid, enol-citronellal acetate is inverted into isopulegol acetate (b. p. 100 to 105° [10 mm.]; $d_{20°}$ 0,925; $[\alpha]_D$ about 0°; n_D 1,459).



Citronellal



Citronellal enol-acetate



Isopulegol acetate

Citronellal and cinnamic aldehyde. A paper by W. Kerp and P. Wöhler[1]), which has been published by the Imperial Department of Hygiene, makes a contribution to the knowledge of the combinations of sulphurous acid with citronellal and cinnamic aldehyde. The paper is a continuation of researches[2]) into the analogous compounds of formaldehyde, acetaldehyde, benzaldehyde, acetone, and glucose. The bodies which must be regarded as sodium salts of α-hydroxysulphonic acids, as is well known, can be prepared without difficulty and are as readily broken up again into their component parts. The authors, in the course of their investigations, show that this decomposition process already takes place in an aqueous solution at ordinary temperature. The sulphurous acids in combination, such as those of acetaldehyde and glucose in wine and dried fruit, are constant towards oxidising agents, but when aqueous solutions of the sodium salts of all the above-named hydroxysulphonic acids are diluted with iodine-solution, iodine is used up, in other words, oxidation takes place. From this it must be inferred that these combined sulphurous acids and their salts, when in aqueous solution, are in a state of hydrolytical dissociation. This state is independent on the one hand of the power of the bond between sulphurous acid and the aldehydes and ketones, and, on the other, of the temperature and the degree of concentration of the solution. In the case of each of these salts there exists, when it is in aqueous solution, a condition of equilibrium between the non-dissociated part on the one hand and the aldehyde or ketone and the sodium bisulphite on the other, this condition being determined by the temperature and the degree of concentration of the solution. The dissociation increases with a rise in temperature; it diminishes with an increase in concentration. The authors have studied in a similar way the condition of the three theoretically possible products of reaction of citronellal or cinnamic aldehyde with bisulphite, that is to say: citronellal (cinnamic aldehyde) sulphite, citronellal (cinnamic aldehyde)

[1]) Arbeiten a. d. Kaiserl. Ges. Amt **32** (1909), 89.
[2]) Ibidem **21** (1904), 182; **26** (1907), 260.

hydrosulphonate, and citronellal (cinnamic aldehyde) dihydrosulphonite of sodium in aqueous solution. Both salts, viz., citronellal and cinnamic aldehyde sulphite of sodium, according to these investigations, behave differently from the combinations previously investigated, inasmuch as no constant condition of equilibrium occurs in their aqueous solutions under dissociation. In the place thereof there occurs, in addition to the decomposition of the complex of the aldehyde-sulphite-anion into aldehyde- and bisulphite-ion (which at first proceeds normally and depends upon the concentration of the solution) a second reaction. This consists of the addition of the bisulphite-ion to the portion of the complex which has not been decomposed, the corresponding aldehyde-dihydrosulphonic-acid-anion being formed. Compared with the second, the first reaction proceeds rapidly, so that in practice equilibrium of the decomposing-complex may be assumed to exist at any time. In the case of citronellal and in agreement with its greater molecular weight, the dissociation is greater than it is in the cinnamic aldehyde complex. The complex of the citronellal hydrosulphonic salt does not decompose in aqueous solution: it is therefore a thoroughly stable compound. The same may be the case with the cinnamic aldehyde hydrosulphonic compound. As the latter could not be kept in pure analytical form, the phenyl sulphopropionic acid salt was examined in lieu of it for its behaviour in aqueous solution, and was found to be quite stable. On the other hand the decomposition of the complex of the dihydrosulphonic salts of the two aldehydes is normal, although very slight. In this case the molecule of sulphurous acid which has been added to the double-bond has a certain protective action upon the sulphurous acid which has been added to the aldehyde group, by considerably retarding its abstraction. The addition of the sulphurous acid to the double bond of the aldehyde-sulphite-complex therefore renders the complex considerably more stable.

Citral. Enklaar[1]) had already observed that citral, when reduced by Sabatier's method, yields a series of cyclic as well as of aliphatic products. But, as stated by Skita[2]), the reaction proceeds somewhat differently when palladium chloride and hydrogen are employed; in this case citral gives, besides citronellal and citronellol, a dimolecular aldehyde. The process takes place in the following manner: the reducing agent, in alcoholic solution, is mixed with an aqueous solution of palladium chloride and gum arabic so as to produce a clear solution. Hydrogen is forced into this solution by pressure.

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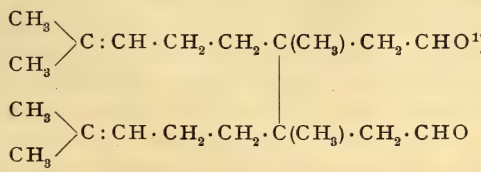
[1]) Chem. Weekblad **4** (1907), 322; Report October **1907**, 113.
[2]) Berl. Berichte **42** (1909), 1633.

First of all the palladium chloride is reduced, after which pronounced absorption of hydrogen is observed. Out of the mass which has resulted from the process of reduction a limpid oil, m. p. 106 to 108° (15 mm.) could be isolated by distillation. This oil gave aldehyde-reactions and yielded a semicarbazone (m. p. ?). Analysis showed that it was probably citronellal. A second fraction boiling from 116 to 118° (15 mm.), gave no aldehyde reactions. It was possible to show by analysis that citronellol had been formed by the absorption of four hydrogen-atoms.

In the process of reduction of citral it may therefore be taken for granted that the dissolution of the α,β-double-bond is first accomplished, and after this the reduction of the aldehyde-group, while the 6,7-double-bond remains intact. A third fraction boiled at 139 to 140° (15 mm.) and formed a viscous oil, which quickly congealed in crystals. Recrystallised from alcohol, this body had a m. p. of 57°. The fuchsine-test revealed the presence of an aldehyde-group. The high b. p. rendered it improbable that a mono-molecular aldehyde was here present. Determination of the molecular weight by the cryoscopic method gave the figure 326,7, whereas the calculation for the di-molecular aldehyde $C_{20}H_{34}O_2$ was 306. A further proof was afforded by analysis of the semicarbazone.

Hence Skita assumes this body to be an aldehyde-analogon of the bi-molecular ketones which have been obtained by Harries from α,β-unsaturated ketones, and assigns to it for the first the following formula



In the same way, β-cyclocitral, the cyclical analogon of citral, gave as sole product of reaction the as yet unknown trimethyl-1, 1,3-hexahydro-benzaldehyde-2.

β-Cyclocitral — Trimethyl-1, 1, 3-hexahydrobenzaldehyde-2

[1]) In the original paper the bimolecular linking has been erroneously joined to the C-atoms (2).

This constituted a liquid of a menthone-like odour, boiling at 58 to 60° (10 mm.), giving aldehyde-reactions with silver-salts and fuchsine-solution, and yielding a solid semicarbazone of which the m. p. is not stated.

A series of other bodies was also obtained by reduction, but these lie outside our special branch and are therefore of no interest to us.

On the determination of citral, see Analytical Notes, p. 152.

Pinonic aldehyde. Some time ago, Harries[1]) expressed the surmise that when pinene ozonide is decomposed by heating it with water, there is formed, in addition to pinonic acid, an aldehyde which is probably pinonic aldehyde. A fresh investigation conducted by C. Harries and H. von Splawa-Neyman[2]) has established the fact that the decomposition of the hydroaromatic ozonides can be more easily carried out by warming with glacial acetic acid than with water, and that, if this is done in the case mentioned above, the formation of the assumed pinonic aldehyde is facilitated. Pinene ozonide was heated with acetic acid on the water-bath to 90°, and the residue (after evaporating the acetic acid *in vacuo*) was fractionated. A fraction boiling between 100 and 142° (12 mm.), which strongly reduced ammoniacal solution of silver and Fehling's solution, formed a semicarbazone, m. p. 214 to 215°. Analysis showed this to be a di-semicarbazone, probably that of pinonic aldehyde, $C_{10}H_{16}O_2$.

Piperonal. Pauly and Alexander[3]) have again investigated the body known as dichloro-piperonal, which according to the latest researches is to be definitely regarded as a carbonate of 3,4-dihydroxybenzalchloride. An attempt was made to saponify the body into the corresponding pyrocatechol, but in this process protocatechuic aldehyde was always formed. Only by saponification with the theoretically required quantity of water in the presence of dry pyridin no aldehyde was obtained, but in lieu thereof there was formed a coloured chlorinated body which could not be obtained in the pure state and which gave the impression of being a pyridinium compound. The readiness with which the two chlorine atoms react is ascribed by the authors as connected with the mobility of chlorine atoms in the presence of a phenolic hydroxyl group in para position which has been observed by various investigators, inasmuch as aldehyde formation also occurred when only the para-hydroxyl of dichloropiperonal was liberated, as in the saponification with pyridin (or sodium acetate) in a methyl-alcoholic solution, in which the monomethyl carbonate of protocatechuic aldehyde, $C_6H_3\begin{cases}(1)CHO\\(3)O\cdot CO\cdot OCH_3\\(4)OH\end{cases}$,

[1]) Berl. Berichte **41** (1908), 38; Report April **1908**, 178.
[2]) Berl. Berichte **42** (1909), 879.
[3]) Berl. Berichte **42** (1909), 2350.

is formed in the shape of fine needles, m. p. 93°. On the other hand, an attempt to obtain from "dichloro-piperonal" the corresponding glycol diacetate $CO \cdot O_2 \cdot C_6H_3 \cdot CH \cdot (OCOCH_3)_2$ by means of acetate of silver, proved the chlorine atoms to be linked comparatively firmly. The expected body, which crystallised out in warts (m. p. 84,5 to 85°) from ligroin-benzene could only be readily obtained by boiling dichloro-piperonal with acetate of silver and acetic anhydride for several hours.

The reduction of "dichloro-piperonal" by zinc dust and glacial acetic acid, which proves its constitution, and which had been carried out previously, yields almost 90 per cent. of the theoretical quantity of homo-pyrocatechol carbonate when the following method is applied: instead of dissolving the concentrated acid solution in water and neutralising it with soda when the process of reduction is completed, the residue is dissolved in chloroform, the glacial acetic acid still remaining is repeatedly extracted with water until the acid reaction has ceased; and after drying the solvent is evaporated and the residue distilled *in vacuo*. Under certain conditions, when completely anhydrous glacial acetic acid is used and the operation is conducted in the cold way, it is possible, by adding known quantities of zinc dust, to carry the reduction only up to the point where the carbonate of the 3,4-dihydroxy-benzylchloride $CO \cdot O_2 \cdot C_6H_3 \cdot CH_2Cl$ (lustrous needles, m. p. 53,5 to 54°, from ligroin) is formed. Boiled with acetate of silver and acetic anhydride, this body yielded the corresponding carbonate of the 3,4-di-hydroxy-benzylalcohol, m. p. 59,5°. With pyridin and the required volume of water, the theoretical quantity of carbonic acid was split off from the carbonate, but with simultaneous formation of a pyridinium-compound, probably of the following formula: $(HO)_2 \cdot C_6H_3 \cdot CH_2N(Cl) : C_5H_5$ melting between 170 and 171°.

Ketones.

Methyl-heptenone. It has been stated by Verley[1]) that when methyl-heptenone is heated with sulphuric acid as a dehydrating agent, it yields 1,3-dimethyl cyclohexadiene.

In order to prepare this compound, W. Crossley and N. Renouf[2]) heated methyl-heptenone with sulphuric acid, but in doing so they obtained a hydrocarbon which boiled somewhat inconstantly at from 130 at 132° and of which the analytical constants pointed to a mixture of dimethyl-cyclohexadiene and dimethyl-cyclohexane. The same result was observed when chloride of zinc and phosphorus pentoxide were used. Wallach had informed the authors that the hydrocarbon which is formed when water is eliminated from methyl-heptenone is

[1]) Bull. Soc. Chim. III. **17** (1897), 180; Report April **1897**, 53.
[2]) Journ. chem. Soc. **95** (1909), 930.

not homogeneous[1]), because a good deal of m-xylene is formed as a bye-product. No free hydrogen is formed; this being probably consumed in the reduction of the dimethyl-cyclohexadiene to dimethyl-cyclohexane. As Wallach himself is engaged in further research on this subject, Crossley and Renouf content themselves with communicating the results of their unfinished experiments.

Upon oxidising the hydrocarbons with 4 % aqueous solution of permanganate of potassium they obtained m-xylene (b. p. 136 to 139°; b. p. of the trinitro compound 182°), *iso*phthalic acid (m. p. of the methyl ester 64 to 65°), a volatile acid (probably acetic acid), and a ketonic acid. Oxidation with permanganate of potassium in acetone solution resulted in a body $C_8H_{16}O_2$ melting at 90° and probably representing the glycol mentioned by Wallach (*loc. cit.*) as well as of another neutral product with a low m. p., which was not further examined. Besides these, the investigators obtained a ketone or ketonic acid. The corresponding semicarbazone melted at 129 to 131°, but the molten substance only became quite clear at 182°.

Crossley and Renouf conclude from their investigations that the hydrocarbon which is formed from methyl-heptenone by abstracting water contains considerable proportions of m-xylene and dimethyl-cyclohexane, and probably not more than 30 to 40 % of dimethyl-cyclohexadiene.

Carvone. As is well known, three carvoximes (d-, l- and i-oxime) have been prepared, and these may be obtained from the carvones by the action of hydroxylamine and from limonene nitroso-chlorides by the splitting off hydrochloric acid. Deussen[2]) has recently obtained a new carvoxime in the course of converting d-limonene nitroso-chloride into l-carvoxime by acting upon it with one molecule of sodium methylate. The oil which was formed in this process was freed from carvoxime crystals, distilled *in vacuo* and analysed. The analytical values agreed for an oxime $C_{10}H_{14}$:NOH. As the rotation was changeable, Deussen supposed that, in addition to l-carvoxime, there was present an as yet unknown dextrorotatory oxime. As a matter of fact, it was possible to separate the oximes by conversion into the benzoyl-compound, the benzoyl-compound of l-carvoxime in cold ligroin being less soluble than that of the new oxime. Recrystallised from dilute alcohol, the new benzoyl carvoxime showed the following constants: m. p. 77°, $[\alpha]_D$ + 75,3° (in benzene). The new d-carvoxime recovered from the benzoyl-compound, after having been

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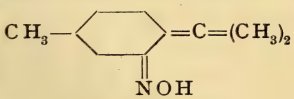
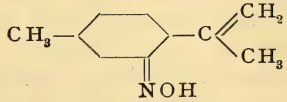
[1]) Compare Wallach: *Terpene und Campher*, p. 351, Leipzig, Veit & Co. 1909.
[2]) Zeitschr. f. Riech- und Geschmackstoffe **1** (1909), 25; through Chem. Zentralbl. **1909**, I. 1237.

recrystallised from dilute alcohol, formed lustrous needles possessing the following properties: m. p. 57 to 58°, $[\alpha]_D$ + 68,3° (in benzene); very readily soluble in the usual organic solvents. When heated with dilute sulphuric acid an oil with a clearly-defined odour of carvone was obtained. The author proposes to distinguish the new carvoxime as β-carvoxime and the already known lævorotatory body, m. p. 72°, as α-carvoxime.

Pulegone. So far, a series of observations on the properties and behaviour of normal pulegone oxime have been available, from which it is evident that the constitution of this body has been by no means cleared up[1]). Wallach, who had already previously reported on normally-constituted pulegone oxime[2]), has recently repeated his experiments[3]). He heated pulegone with hydroxylamine hydrochloride in alkaline solution for 10 minutes, and from the mass resulting from the reaction he obtained, by distillation *in vacuo*, three fractions, which respectively proved to be acetoxime, methylcyclohexanone oxime and pulegone oxime. The last-named body could only be purified with difficulty; only after repeated recrystallisation from methyl alcohol was the m. p. brought to 123 to 124°. Its specific rotatory power was $[\alpha]_{D\,22°}$ — 25,833° in a 6,43 per cent. solution of methyl alcohol. When the oxime was boiled with diluted sulphuric acid a substance which appeared to be pulegone was recovered from it. But as the semicarbazone which was prepared from the pulegone, when recovered in different experiments, did not possess a uniform m. p., decomposition with oxalic acid was resorted to, and this process showed that the ketone recovered was not pulegone, as had been accepted, but *iso*-pulegone. The semicarbazone of the *iso*-pulegone melted at 172 to 173°. The compound which has hitherto been regarded as pulegone-oxime is therefore actually *iso*-pulegone oxime.



Pulegone oxime



*Iso*pulegone oxime

In order to make a comparison *iso*-pulegone was prepared from pulegone hydrobromide by Harries' process[4]) and the oxime of this was found to be identical with that from the pulegone referred to above: m. p. 121°, $[\alpha]_{D\,18°}$ — 26,20°.

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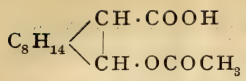
[1]) Report April **1897**, 56; October **1898**, 52.
[2]) Liebigs Annalen **277** (1893), 160; **289** (1895), 347.
[3]) Liebigs Annalen **365** (1909), 240.
[4]) Berl. Berichte **32** (1899), 3368; Report April **1900**, 64.

Furthermore, citronellal was converted by Tiemann's and Schmidt's method into *iso*-pulegol and the latter into *iso*-pulegone; in this case also the oxime was identical with that obtained from pulegone. In the course of the last-named manipulation two oximes were formed, both of which, contrary to the results obtained by Tiemann and Schmidt, volatilised with steam, and could only be separated with difficulty into an inactive oxime (m. p. 138 to 139°) and into the active oxime referred to above (m. p. 122°) by recrystallisation from methyl alcohol. In certain circumstances, as shown ay Harries, it is even possible that in the course of the conversion of citronellal only an inactive ketone is formed.

Camphor. The preparation of isomeric borneol carboxylic acids by means of the electro-reduction of camphocarbonic acid was the subject, several years ago, of a short paper by Bredt and Burkheiser[1]). A detailed communication on this reaction and the conversions which are related to it in further sequence has now been published by Bredt[2]) in conjunction with Scheen, Quaritsch, Wornast and Langguth. The apparatus employed for the electrolytic process has been improved in this respect that the spaces for the anodes and cathodes have been separated by a specially arranged diaphragm which makes it possible to keep the cathode-liquid in constant agitation by means of a stirring-rod. A lifting tackle of peculiar and ingenious construction, with lever-movement, and kept at a fixed height by means of a float, keeps the anode-liquid (concentrated potash-solution) at a stable level, while the liquid is protected from heating and evaporation by means of an internal condenser. The termination of the reduction (for which about nine times the theoretical ampères was needed) was indicated by the sharp reaction of camphocarbonic acid with ferric chloride. Even traces of the acid may be detected in the colorimeter by the bluish-green colour. The crude borneol carboxylic acid, of which 88 % of the theoretical yield was recovered, was split up in the two isomerides (m. p. 171° and 101°) already referred to by dissolving the crude acid, which was entirely free from ether, in 1 to $1^1/_2$ times its volume of toluene with the application of heat, and by leaving the solution to stand for 24 hours at the ordinary temperature of the laboratory. In the course of this process the greater part of the acid with m. p. 171° separates out first. By shaking the separated mother-liquor in a freezing-mixture the isomeric borneol carboxylic acid (m. p. 101°) is next separated. Further quantities of both acids may be obtained by leaving the solution to stand alternately at ordinary temperature and by subsequent cooling, if need be after concentrating

[1]) Liebig's Annalen **318** (1906), 199; Report October **1906**, 135.
[2]) Liebig's Annalen **366** (1909), 1.

the too-highly diluted solution. The yield of the two isomerides was as follows: 100 g. camphocarbonic acid, or 90 g. crude borneol carboxylic acid, gave 35 g. acid m. p. 171°, and 40 to 50 g. acid m. p. 101°. The residue of 10 to 15 g. acid mixture remaining in the mother liquors was afterwards treated for bornylene carboxylic acid. From the toluene which had served for the purification of the two acids, an acid melting at 126° could be isolated, which may either represent a new isomeride, or possibly a eutectic mixture of the two known acids. From the fact that the two last-named, when oxidised with nitric acid, were converted into camphoric acid, the conclusion might be drawn that the question at issue was only one of stereomery. By means of dehydration the two modifications could also be converted in the same unsaturated acid, viz., bornylene carboxylic acid (known at the time as dehydroborneol or camphene carboxylic acid), although not equally ready; the acid melting at 171° yielded its unsaturated acid rather less readily than the acid of m. p. 101°. Hence, Bredt designates the last-named acid *cis*, and the first-named *cis-trans*, borneol carboxylic acid. The two isomerides are further differentiated by the fact that the *cis* acid yields a calcium salt which contains water of crystallisation, is more sparingly soluble in hot than in cold water, and when oxidised with permanganate yields camphoric acid, m. p. 186°; while the *cis-trans* acid gives an anhydrous calcium salt of normal solubility and remains unchanged when oxidised with permanganate. As already stated, both acids, when oxidised with nitric acid, are converted into camphoric acid. Their behaviour towards acetyl chloride is likewise the same in all essentials (the *cis-trans* acid, with its high m. p. only reacting when heated, the *cis* acid reacting without heat) and the same products are formed, partly acid, partly neutral, according to the quantity of acetyl chloride employed. Treated with only two parts of this reagent both acids yield the same acetate I, m. p. 122 to 123°; but when this is saponified only *cis-trans* acid (m. p. 171°) is regenerated, indicating a conversion of the *cis*-variety into the *cis-trans* isomeride. When treated with four parts of acetyl chloride both acids yield a mixture of two indifferent products, consisting (as concluded from the decomposition-products yielded by dry distillation), of a mixture of the anhydride II of the acetylated acid I, which, when distilled, is split up into acetic acid and bornylene carboxylic anhydride III (m. p. 97°, b. p. 220° to 225°, 15 mm.) and of a lactide-like anhydride IV, viz., *cis-trans* borneol carboxylic acid. The latter, when distilled, is converted into two molecules of bornylene carboxylic acid V (m. p. 112 to 113°; b. p. 158° at 13 mm.). The latter acid could also be obtained by the slow distillation of two borneol carboxylic acids *in vacuo*, but it can be prepared more advantageously from the acetylation-products referred to.



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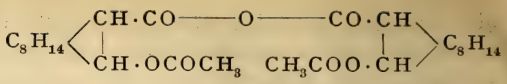

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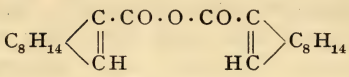

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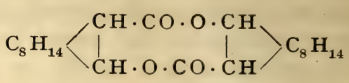

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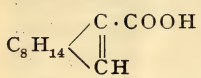

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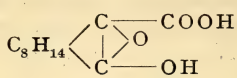
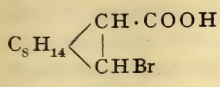


VI

By oxidising bornylene carboxylic acid with permanganate, it was shown that the unsaturated acid is a carboxylic acid of bornylene, and not (as at first surmised) of camphene, and that the splitting-off of water consequently takes place in a normal direction and without rearrangement. This reaction yielded, in addition to camphoric acid (soluble in ether); hydroxy-oxide-camphane-carboxylic acid VI, m. p. 208 to 209°, insoluble in ether. On the other hand, oxidation with nitric acid only led to camphoric acid. As an unsaturated acid, bornylene carboxylic acid united with hydrohalogens; its behaviour towards hydrobromic acid was investigated closely, less closely that towards hydrogen chloride. When treated with glacial acetic acid-hydrobromic acid, the principal resultant product was β-hydrobromo bornylene carboxylic acid VII (β-bromo-camphanic carboxylic acid) m. p. 90 to 91°, together with a compound called a hydroxy-acid, $C_{11}H_{18}O_3$ m. p. 169°. These bodies, owing to the sparing solubility of the sodium salt of the brominated acid, were separable in cold concentrated soda solution. Nothing is reported as to the structure of the supposed hydroxy-acid. It is not identical with any of the borneol carboxylic acids and therefore (as was proved by special experiments) it cannot have been formed from the brominated acid by the interchange of Br for OH. When its aqueous solution was boiled with reflux-condenser this hydroxy-acid was converted into a dehydrated acid, m. p. 55°, which volatilised with steam and was an isomeride of bornylene carboxylic acid. The addition of hydrogen chloride to bornylene carboxylic acid in a solution of glacial acetic acid proceeds in analogous manner: besides the hydroxy-acid mentioned already (m. p. 169°) there is formed β-hydrochloro-bornylene carboxylic acid, m. p. 84 to 85°. But the action of aqueous hydrobromic acid upon the unsaturated acid takes a different course: in this case the chief product formed is α-brominated acid VIII m. p. 157° with very little of the β-brominated acid VII. The acid with a high m. p. was recognised as α-bromo-substituted acid by the

fact that when boiled with aqueous alkali-carbonate it was readily converted into an isomeric borneol carboxylic acid m. p. 176° which differed likewise from the two original borneol carboxylic acids, and when oxidised with nitric acid yielded no camphoric acid.



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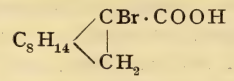

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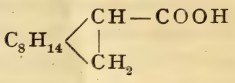

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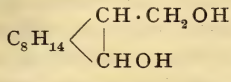

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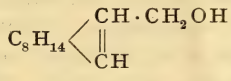
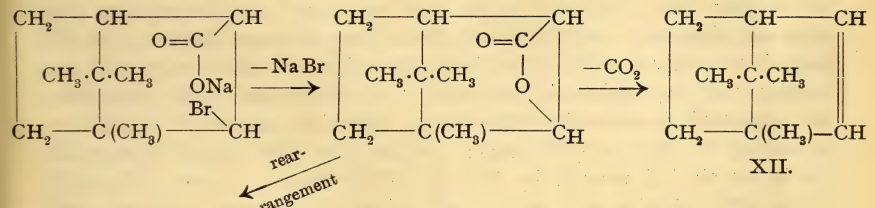


XIV.

When the β-brominated acid, m. p. 90 to 91° was treated with alkali the result differed according to the quantity of alkali used. Analogous to β-hydrobromo cinnaminate of sodium, the sodium salt of the acid, treated in a neutral aqueous solution, forms bornylene and bornylene carboxylic acid, but the chief product of the conversion is a lactone $C_{11}H_{16}O_2$, m. p. 183°, b. p. 145 to 147° (12 mm.), of peculiar constitution. The yield of this lactone is considerably raised when the solution is made alkaline. This product has been recognised as γ-hydroxy-carbohydrocamphenic acid lactone IX and, on the assumption that a rearrangement takes place, its formation would be explained by the following formulae: —



XII.

IX.

X.

Bredt argues from various indications that the rearrangement in question, i. e. the displacement of the halogen from the β- into the γ-position, occurs during the boiling of the aqueous solution of the sodium β-hydrobromo or β-hydrochloro bornylene carboxylate. The constitution of the lactone was determined by its oxidation into

hydroxycamphenilane- (camphenilol) di-carboxylic acid lactone X, m. p. 230°, and of the calcium and barium salts of the latter.

The reduction of the β-hydrobromo bornylene carboxylic acid with potassium-amalgam led, as a result of the ready displacement of the bromine-atom by hydrogen, to ortho-camphane carboxylic acid XI, m. p. 90 to 91°, b. p. (13 mm.) 153°. But similar treatment of the α-brominated acid yielded the same hydroxy-acid which had been formed during the treatment with alkali carbonate; it therefore underwent no reduction. On the other hand, reduction with zinc and hydrochloric acid in glacial acetic acid solution yielded an acid free from bromine, m. p. 209°. This acid, which has not been further investigated up to the present, may be surmised to be the hydrated acid which was looked for.

The object of the examination of the bornylene XII, formed by treating β-bornylene carboxylic acid with alkali, was to determine the uniform character of this terpene. This body, which is of quite exceptional volatility and passes over quite easily even with ether-vapour, was found to possess the following constants: m. p. 113°, b. p. 146° at 740 mm., $[\alpha]_D$ in methyl alcohol — 26,96°, in toluene — 21,69°. Hence the dextro-rotatory testing material had yielded a body of the opposite rotation, a circumstance of which other examples were already on record. Judging by its high m. p. the bornylene thus obtained was considerably purer than the terpene prepared from bornyl iodide by Wagner and Brickner, which had m. p. 97°, and also than the terpene obtained by Tchugaeff from bornyl xanthogenate, which melted at 103 to 104°. The body from bornyl iodide may perhaps contain not inconsiderable proportions of camphene, which can only be separated imperfectly from each other by means of hydration according to Bertram-Walbaum's process (by this method bornylene yields an alcohol termed by Wagner β-borneol, m. p. 203 to 204°). Tchugaeff's terpene was rather less impure, and was converted into camphoric acid, m. p. 186°, by oxidation with a 1% aqueous solution of permanganate.

In a further paper Bredt and Sandkuhl[1]) deal with the relations of the camphyl glycols to the borneol carboxylic acids; a subject which has also been touched upon in the previous communication. The method of preparing the alleged inseparable mixture of *cis*- and *cis-trans*-camphyl-glycol XIII was improved, as was also the method of obtaining the primery material (hydroxy-methylene camphor), and for the separation of both stereomeric modifications fractional crystallisation from acetic ester was employed. The *cis*-glycol, from which water

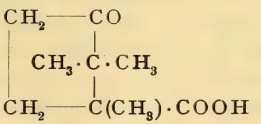
[1]) Liebig's Annalen **366** (1909), 62; see also Report October **1906**, 135.

splits off readily, separated out first in the shape of clear crystalline needles, m. p. 87°. When left to stand for some time longer, there separated out from the solution masses of a porcelain-like appearance. On one occasion such a solution of the glycol mixture yielded a large crystal, melting at 96°, which may have represented either a eutectic mixture of both forms, or a third stereomeric variety. The *cis-trans*-glycol was prepared in the usual way by treating the residue of the acetic ester solution, which contains both glycols, in benzene solution with hydrochloric acid gas, with application of heat. By this treatment the *cis*-camphyl glycol which is still present is converted into dehydro-camphyl glycol = bornylene carbinol XIV, m. p. 67 to 68° (this body volatilises with steam); while the stable *cis-trans*-glycol remains as a residue of steam-distillation and is isolated in the familiar manner.

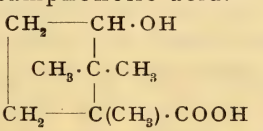
Oxidation of the two glycols with permanganate elucidated the relations of each to the different borneol carboxylic acids. Corresponding to the different behaviour of both acids during this oxidation process, the glycols, too, yielded different products of oxidation, that is to say, *cis-trans*-camphyl glycol (m. p. 118°) yielded 84 per cent. of the higher melting *cis-trans*-borneol carboxylic acid, while *cis*-camphyl glycol (m. p. 87°) yielded camphoric acid. In the case of the latter, however, either through conversion into the *cis-trans*-variety, but more probably because of the impure state of the *cis*-glycol, a small quantity of *cis-trans* borneol carboxylic acid was also produced. Hence, so far as concerns their relationship as glycol and hydroxy acid, the following are related: —

Cis-camphyl glycol, m. p. 87°, and *cis*-borneol carboxylic acid, m. p. 101°; *cis-trans*-camphyl glycol, m. p. 118°, and *cis-trans*-borneol carboxylic acid, m. p. 171°.

Bredt attaches to both papers a footnote communicating that camphononic acid,



which up to the present could not even be reduced by sodium in a solution of boiling amylalcohol solution, was converted by electrolysis into the corresponding camphonolic acid:



m. p. 197 to 198°, and the latter, by the elimination of water, into the corresponding camphonolic lactone, m. p. 161°.

Before the Société chimique de France, G. Blanc[1]), the French chemist who has made himself well-known as a successful investigator in the domain of camphor and allied compounds, read a paper on the History of the Research into the Constitution of Camphor, which, in its essence, runs on parallel lines with the history of the synthesis of camphoric acid, the principal derivative of camphor. The very detailed paper of course deals only with known facts in historical order, and it is therefore unnecessary for us to enter into particulars of it, but we desire to correct some of the author's statements. Blanc does not do justice to the sequence of events when he traces the establishment of Bredt's camphor-formula, (which apparently he acknowledges with some reluctance) to the formation of dimethyl malonic acid from camphoric acid observed by Koenigs. Apart from the circumstance that Bredt had already published the facts from which he deduced his formula before Koenigs' paper appeared[2]), that formula was based upon Bredt's own observation, (subsequently elaborated by A. Helle in the form of a dissertation,) that the first decomposition-product of camphoric acid, viz., camphoronic acid, is split up by dry distillation into trimethyl succinic acid, *iso*butyric acid, carbon dioxide, water, and carbon[3]). Nor is the assertion well-founded that Bredt did not adduce a shadow of proof in support of his theory. That scientist, on the contrary, most clearly stated and proved by experiment that certain properties of camphoric acid and of homocamphoric acid, such as the formation of anhydride, the caloric value, etc, must needs lead to the conclusion that the former acid was a substituted glutaric acid, and the latter an adipic acid. These views, it is true, could not be brought into harmony with Bouveault's formula so warmly championed by Blanc at the time. On the occasion of the well-known debate at the *Naturforscherversammlung* at Brunswick, Bredt finally disproved the correctness of Tiemann's camphor formula. Bredt at first then pointed to the parallellism of the conversion of α-campholenic acid and of α-campholytic acid into the corresponding β-isomerides, and thereby cleared up a contradiction which had been observed, but not explained, by Blanc himself. It will be sufficient merely to quote these achievements of Bredt. It would be difficult to understand how Blanc could maintain that it was partly the opponents of Bredt's formula who afforded the proofs of its correctness, if to this assertion he had not added the sentence: *"ceci dit uniquement pour montrer que la manifestation de la vérité prime toute considération"*. This shows how hard Blanc finds it to acknowledge Bredt's formula.

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[1]) Bull. Soc. chim. IV. **5** (1909), Supplement to No. 9 of May 5th.
[2]) Berl. Berichte **26** (1893), 2337.
[3]) Berl. Berichte **26** (1893), 3047.

The synthesis of camphoric acid carried out by Komppa[1]), Blanc regards as illusory, in the first place because, upon repetition of the process, the very first reaction (preparation of diketoapocamphoric acid) was already a failure, secondly because Komppa has neglected to follow up his preliminary communication, which was made nearly six years ago, by a detailed publication. No doubt Komppa will himself make a rejoinder to an attack delivered in such an unusual manner.

In conclusion Blanc asserts that the only problem in the chemistry of camphor which yet remains to be cleared up is the conversion of camphor into camphene and *vice-versâ*, and hints that perhaps he himself will take up this difficult question at a later date.

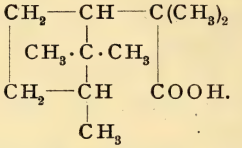
Up to the present the only known homologues of camphor are the monoalkyl compounds which have been prepared by various methods by Baubigny, Minguin, and others. By treating sodium-camphor (from camphor and sodium amide) with methyl iodide in solution of ether or benzene, Haller and Bauer[2]) obtained dimethyl camphor $C_8H_{14}\begin{cases}C(CH_3)_2\\ |\\ CO\end{cases}$ which was recovered, in addition to about 25% of the weight of monomethyl camphor, from the product of the above-mentioned conversion (b. p. 96 to 105°, 11 mm.) and which was separated from the latter by converting this into its oxime. The pure dimethyl camphor boiled at 106° (14 mm.) as a colourless liquid, with an odour of camphor and fenchone. It possessed the following constants: $d\frac{15°}{4°}$ 0,94708, $[\alpha]_{D24°}$ + 92,7°, in alcoholic solution + 92,5°, mol. refr. found 53,21, calc. for $C_{12}H_{20}O''$ 53,31, $M_\gamma - M_\alpha$ found 1,30, calc. 1,27. The oxime of monomethyl camphor, prepared by Crismer's method with zinc chloride and hydroxylamine hydrochloride had a much higher b. p. than dimethyl-camphor (134 to 135° 11 mm.) and could therefore easily be separated. Reduction of the last-named body with sodium in a solution of absolute alcohol led to dimethyl borneol, a viscous mass with a pronounced odour of borneol, congealing in the cold; m. p. 18 to 20°; b. p. 109 to 111° (13 mm.). A few crystals, m. p. 28 to 30°, with a rotation $[\alpha]_D$ + 32,4° appeared to be a mixture of the two stereomeric dimethyl borneols. The urethane of the new borneol crystallised in the shape of small needles, m. p. 111,5 to 112°, soluble in alcohol and ether, insoluble in petroleum-ether, $[\alpha]_D$ + 29,5°.

When dimethyl camphor was further treated with sodium amide in a hot solution of benzene the well-known disruption of one of the

[1]) Comp. Report April **1904**, 98.
[2]) Compt. rend. **148** (1909), 1643.

pentamethylene-rings took place, and resulted in the formation of the amide of dimethyl campholic acid, $C_8H_{14}\begin{cases}CH(CH_3)_2\\CONH_2\end{cases}$, b.p. 179 to 180° (14 mm.); m. p. 72 to 73°; $[\alpha]_D$ in alcoholic solution + 70,8°. The free acid which (like all trialkyl acetic acids), could not be prepared from the amide by saponification with potash, was obtained from the sulphuric acid solution of the amide by treatment with sodium nitrite solution and heating to about 60°. The acid, which was very readily soluble, melted at 73 to 74°; $[\alpha]_D$ + 47,4°.

In order to ascertain the place where the pentacyclic ring had opened the acid was oxidised with permanganate, as besides resulting in the acid mentioned above, the disruption of the ring might also have resulted in an acid



In the event of the disruption having resulted in an acid of the first-mentioned formula, the tertiary H-atom at the dimethylated C-atom should be converted into hydroxyl, and, by the splitting-off of water, a dimethyl campholide $C_8H_{14}\begin{cases}C(CH_3)_2\\ \\CO\end{cases}O$ be formed, which, upon further oxidation, should yield camphoric acid. An acid of the second formula could not yield camphoric acid when oxidised. The experiment resulted in an acid which differed from camphoric acid, and from which carbon dioxide was given off when heated. But owing to its scarcity it was impossible to identify this acid.

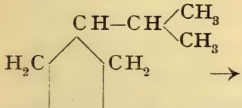
The authors intend to continue their research into this reaction, especially as regards the formation of methyl camphor, methyl borneol and the higher alkylated homologues of these two bodies. As stated above, the dialkylated derivatives can be separated from their mono-alkylated homologues.

Fenchone. Bouveault and Levallois [1]) have continued their research on the synthesis of fenchone and its derivatives [2]). In a previous publication, Bouveault and Blanc [3]) had already demonstrated that the only difference between fenchone and camphenilone, and between di-

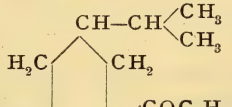
[1]) Comp. Report April **1908**, 189.
[2]) Compt. rend. **148** (1909), 1399 and 1524.
[3]) Comp. Report April **1908**, 191.

hydro-camphoceenic and dihydro-fencholenic acid lies in one of these bodies possessing one methyl-group more. If, therefore, the hydrogen atom which occupies the α-position towards the carboxyl group were replaced by the methyl-group according to Haller's and Bauer's method, dihydro-fencholenic acid should result.

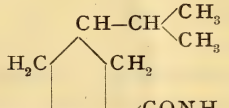
With this object in view the authors converted dihydro-camphoceenic acid into the chloride, a colourless liquid, boiling at 98° (16 mm.) which was condensed with benzene in the presence of chloride of aluminium into 3-benzoyl-1-*iso*propyl-cyclopentane (b. p. 166° at 12 mm.; oxime, m. p. 128°) which, after methylation by heating it with sodium amide in the presence of toluene was split up into benzene and in the amide of 3-methyl-1-*iso*propylcyclopentane-3-carboxylic acid. This synthetic amide must be identical with the racemic dihydrofencholenic acid amide. It agreed, in fact, with that body, except as regards the m. p., which was about 109°, while that of racemic dihydrofencholenic acid amide is about 116°, or, according to Barbier and Grignard, from 114 to 115°.



Dihydrocamphoceenic acid



3-Benzoyl-3-methyl-1-*iso*propylcyclopentane

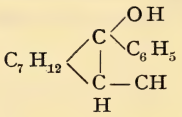


3-Methyl-1-*iso*propylcylopentane-3-carbamide

The authors, at first believing the product to be impure, repeated their experiments, but without achieving any different result. They therefore began to suspect that the amide which they had obtained was an inseparable mixture of the *cis*- and *trans*-modifications. In fact, further investigation showed that the synthetic amide contains racemic amide. The action of sodium hypobromite upon dihydro-fencholene amide from natural fenchone (placed at the author's service by us), resulted in a symmetrical urea, diapofenchyl-urea, m. p. 168°; the racemic amide obtained by mixing the two active amides yielded two isomeric ureas, m. p. 175 and 161°, the synthetic amide yielded of the bodies m. p. 162 to 163° and 136°. The enantiomorphic ureas prepared from d- and l-fenchone melted at 168°; when mixed they yielded a racemic urea, m. p. 185°. This latter was sparingly soluble and when re-congealed melted at 175°. The racemic urea, when heated to 180 to 200°, underwent no outward change, but it then became possible to decompose it by fractional crystallisation from ether into two isomerides, melting at 162 to 163° and at 148°. It was also found possible to separate the mixture of ureas which had its origin in the racemic acids, after heating, by

means of ether into the same isomerides, m. p. 162 to 163° and 148°. The urea melting at 162 to 163° is identical with the one from the synthetic amide with the samo m. p. Therefore the synthetic amide contains the rac. amide looked for.

J. Leroide[1]) has discovered that when fenchone is treated with phenyl-magnesium bromide, compounds are formed which are only with difficulty soluble in ether and in hydrocarbons. When treated with water these bodies yield fenchone and the hydrocarbon corresponding to the aromatic radical. But when these phenyl-magnesium compounds are subjected to prolonged heating with a large quantity of solvent, the magnesium-compounds of the corresponding tertiary alcohols result. For instance, by heating fenchone and phenyl magnesium-bromide for 60 hours in anhydrous ether, Leroide obtained 7 % of tertiary phenyl-fenchyl alcohol



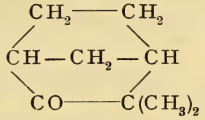
possessing the following constants: m. p. 47°, b. p. 166 to 167° (13 mm.), $[\alpha]_D$ + 45,65° (in alcohol at 18°). He prepared also tertiary p-toluyl-fenchyl alcohol (b. p. 180 to 181° at 15 mm.; $d\frac{15°}{4°}$ 1,0272; $[\alpha]_{D18°}$ 16,30°), and tertiary benzyl-fenchyl alcohol, (long needles m. p. 65 to 66°); b. p. 181 to 182° (15 mm.); $[\alpha]_{D15°}$ + 24,20°.

The action of anhydrous formic acid or acetic acid upon tertiary phenyl-fenchyl alcohol results in the formation of a hydrocarbon with the following properties: b. p. 157 to 158° (13 to 14 mm.); $d\frac{15°}{4°}$ 0,9795, $[\alpha]_{D15°}$ + 0,60°, $n_{j12°}$ 1,5536. When dissolved in glacial acetic acid it absorbs no hydrobromic acid. When treated with bisulphate of potassium a hydrocarbon $C_{16}H_{20}$ is also formed, with the constants: b. p. 139 to 141° (16 mm.); $[\alpha]_D$ + 22,60°; but when this body is dissolved in glacial acetic acid it forms with hydrobromic acid an additive product of hydrobromic acid melting at 115 to 116°. By acting upon tertiary benzyl-fenchyl alcohol with anhydrous formic acid or oxalic acid a mixture is obtained of two hydrocarbons $C_{17}H_{22}$. The principal portion boils at 152 to 154° (14 to 15 mm.); $[\alpha]_{D18°}$ + 71,89°, $n_{j19°}$ 1,5472. The smaller portion has the following constants: b. p. 163 to 166° (14 mm.), $[\alpha]_{D18°}$ 35,33°, $n_{j19°}$ 1,5694. With bisulphate of potassium the same hydrocarbons are obtained, but in this case the principal portion is lævorotatory. Neither hydrobromic nor hydrochloric acid is attached. After allowing ozone in

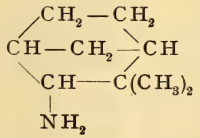
[1]) Compt. rend. **148** (1909), 1611.

chloroform solution to act upon it, the product of reaction, when treated with bisulphite, was found to contain benzaldehyde. In the portion which did not react with bisulphite, benzaldehyde was found present as well as fenchone, the latter being identified from the semicarbazone, m. p. 179 to 181°. From these data Leroide concludes that the hydrocarbon which boils at 152 to 154° represents benzal-hydrofenchene $C_{10}H_{16} : CH \cdot C_6H_5$.

Camphenilone. The formula originally given by Wagner[1]) for this ketone[2]) which appears in the process of oxidising camphene



has subsequently been confirmed by Semmler[3]) and others. Komppa[4]) has prepared a series of derivatives of this ketone (most of which are new), by reducing camphenilone with sodium and alcohol to the corresponding alcohol, camphenilol, m. p. 84° and converting the latter into its acetate (b. p. 95 to 97° (17 mm.); $d\frac{20°}{4°}$ 0,9974; $n_{D20°}$ 1,4628; mol. refr. determined 50,241, calculated for the saturated bicyclical compound $C_{11}H_{18}O_2$ 50,399); its phenyl urethane (needles of m. p. 99,5°) and its acid phthalate (small crystals, m. p. 148,5 to 149°). From the oxime prepared from camphenilone according to Auwers' method (the m. p. of which was found to be 105,5°) it was possible to obtain, by reducing with sodium and absolute alcohol at water-bath temperature, distilling by steam, neutralising the distillate with hydrochloric acid and evaporating to dryness, the hydrochloride of the unknown camphenilyl amine



in the shape of long, thick needles, readily soluble in ether and not melting at 200°. As bye-product, the nitrile of camphoceenic acid was formed, resulting from the action of the hydrochloric acid upon the unchanged oxime; it could be separated from the amine hydrochloride by steam distillation. The free base of the last-named body was liberated by decomposing with an excess of 50 per cent. aqueous potash

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[1]) Chem. Zentralbl. **1897**, I. 1056.
[2]) Comp. Report October **1899**, 62.
[3]) Berl. Berichte **39** (1906), 2577; **42** (1909), 246; Report April **1909**, 121.
[4]) Liebig's Annalen **366** (1909), 71 (1st treatise).

liquor. After dissolving in ether and evaporating the solvent, the base, when distilled in hydrogen current passed over at 185 to 185,5°; congealing immediately into a camphoraceous crystalline mass of powerful smell, reminding of raw, slightly decomposing fish-intestines and also slightly, of bornylamine. The base readily attracted atmospheric carbon dioxide. In a sealed tube it melted at 90 to 92°, and the following derivatives were obtained from it: a double salt of platinum chloride in pale yellow, thin tetrahedra, which turned black but did not melt at 230 to 235°; a picrate in yellow needles, m. p. 205 to 207°, a urea in glassy lustrous small needles, m. p. 167,5 to 168°, and a phenyl sulpho-urea in quadratic prisms., m. p. 154°.

Phenols and Phenol Ethers.

In a previous Report[1]) we discussed the differences discovered by Semmler in the behaviour of the propenyl- and allyl-compounds towards formic acid; propenyl-compounds, such as anethol, becoming completely resinified when boiled with this acid, while the allyl-compounds are not attacked. In connection with this matter, Balbiano[2]) calls attention to a paper which was published by him some time ago, and then commented upon by us[3]). In this paper he described the differences in the behaviour of allyl- and propenyl-compounds towards mercuric acetate, and he has now worked out this subject up to the point of a separation-method. When a cold saturated solution of mercuric acetate is allowed to act upon allyl-compounds, the result is the formation of aceto-mercuric additive products of the formula $R \cdot C_3H_5 \cdot Hg(OH) \cdot C_2H_3O_2$, while propenyl-compounds yield the corresponding glycols $R \cdot C_3H_5(OH)_2$, the mercuric acetate being reduced to mercurous acetate or mercury:

$$\begin{aligned} Hg(C_2H_3O_2)_2 + \tfrac{1}{2}H_2O &= HgC_2H_3O_2 + C_2H_4O_2 + OH \\ Hg(C_2H_3O_2)_2 + 2H_2O &= Hg + 2C_2H_4O_2 + 2OH \\ R \cdot C_3H_5 + 2OH &= R \cdot C_3H_5(OH)_2 \end{aligned}$$

Balbiano has now discovered that this reaction can be very easily used to separate a mixture of allyl- and propenyl-compounds. By allowing a known quantity of mercuric acetate to react upon the mixture the aceto-mercuric compound of the allyl-derivatives is formed exclusively; the propenyl-derivative remains unchanged and can therefore be separated, as it is soluble in ether and volatilises with steam. The aceto-mercuric compound of the allyl-derivative, on the other hand, is practically insoluble in ether and does not volatilise with water-vapour. The allyl-derivative can be recovered from the aceto-

[1]) Report November **1908**, 51.
[2]) Berl. Berichte **42** (1909), 1502. From a copy kindly sent to us.
[3]) Berl. Berichte **36** (1903), 3575; Report April **1904**, 100.

mercuric compound by means of hydrogen generated from zinc and soda liquor. By this process mixtures consisting of 5 g. of each of the corresponding allyl- und propenyl-compounds were separated. From anethol and methyl chavicol he recovered 71% of the anethol and about 50% of the methyl chavicol, from a similar mixture of iso-safrol and safrol 70% and 56,4%; from myristicin and isomyristicin 100% and 72% and from apiol and isoapiol 77% and 52,8% respectively.

Anethol. On the action of light upon anethol see Physical Notes, p. 162.

Creosol. This phenol, which possesses the formula $C_6H_3CH_3(1)OCH_3(3)OH(4)$, and is well-known as occurring in ylang-ylang oil[1]), and as forming one of the principal constituents of the pine-tar phenols, has been described in the form of a solid body for the first time in a paper by O. de Vries[2]). It was obtained from "Creosol synth. cryst." supplied by Schuchardt, by submitting that material to repeated fractionation until the sp. gravity of the principal fraction ceased to show an increase. After being frozen-out from liquid air the body solidified and showed the following constants: b. p. 113,5° (22 mm.), m. p. + 5,5°, $d_{25°}^{25°}$ 1,0951, $d_{4°}^{25°}$ 1,0919, $n_{D25°}$ 1,5353, mol. refr. found 39,39, calc. 38,84. Equal molecules of the phenol and of picric acid, dissolved in alcohol, yielded a picrate melting at 112°.

Acids.

The researches of Wallach[3]) on cyclic hydrocarbons with semi-cyclic linkings, to which we have referred on several occasions, all had started from the hydroxy-acids or the esters of hydroxy-acids (I), which are readily accessible from cyclic ketones by bromoacetic-ester synthesis. By splitting off water these hydroxy-acids yield a double series of acids with isomeric linkings (II, III). But whereas up to the present first the one and then the other of these modifications have been regarded as the principal product, but Wallach[4]) has recently discovered that the occurence of the particular modification is determined by the selection of the dehydrating agent. For instance, cyclohexanol-acetic acid, when treated with bisulphate of potash or pentoxide of phosphorus as dehydrating agents, yields principally Δ^1-cyclohexene-acetic acid; while, if it is treated with acetic acid anhydride, the principal product is the isomeric $\Delta^{1(7)}$-cyclohexene-acetic acid. The esters do not lend themselves so readily

[1]) Report April **1903**, 78.

[2]) Recueil des trav. chim. des P.-B. **28** (1909), 276. From a copy kindly sent to us.

[3]) Report April **1901**, 60; October **1902**, 87; April **1906**, 113; October **1907**, 173; April **1908**, 166; November **1908**, 166.

[4]) Liebig's Annalen **365** (1909), 255.

to splitting-off of water as do the free acids, because in the case of the former certain bodies with high boilingpoints are formed. These bodies, which have not yet been more closely examined, are probably acetyl-compounds.

The unsaturated cyclic acids, both those with a semicyclic and those with a cyclic double-bond, when submitted to dry distillation, give off carbon dioxide and yield identical hydrocarbons in which the double-bond holds the same semicyclic position. This fact supports the already formed theory that in the reaction above referred to the molecule of the hydrocarbons with a cyclic ethylene-bond undergoes a displacement of the double-bond.

It was also noticed that the hydroxy-acid esters are not always readily hydrolisable. The simplest cyclic hydroxy-acids, suc has pentanol-, hexanol-, and p-methyl hexanol-acetic and -propionic acids can be prepared in good proportions in the course of the saponifacation process of the corresponding esters.

The hydroxy-acids remain very stable during the process of saponification, but when subjected to dry distillation they are decomposed at once into carbon dioxide and hydrocarbons; notwithstanding the presence of water the principal products generated are hydrocarbons with semicyclic double-linking. Formerly, only hexacyclic unsaturated hydrocarbons with semicyclic linkings had been converted into ketones with an unsaturated ring, but this conversion-process has now been extended also to pentacyclic systems.

From the large quantity of experimental material which has been published, we select the following details: —

When hexanolacetic acid is boiled with acetic acid anhydride there results $\Delta^{1(7)}$-cyclohexene-acetic acid (m. p. 91°; m. p. of the amide 147 to 148°); a little Δ^{1}-cyclohexene acetic acid is formed as a bye-product. When subjected to dry distillation in a hydrogen-current $\Delta^{1(7)}$-cyclohexene acetic acid methene-hexane (b. p. 103°; $d_{19°}$ 0,802; $n_{D\,19°}$ 1,4499) is formed. 1,4-methyl-cyclohexanone yields by bromo-acetic ester synthesis (after saponification), two modifications of 1,4-methyl-cyclohexanol-acetic acid, viz., an α-acid, m. p. 141° and a β-acid, m. p. 89 to 90°. Both acids, when boiled with acetic acid anhydride, yield 1,4-methyl-cyclohexene acetic acid (m. p. 63 to 64°). The amide forms lustrous flakes, m. p. 121 to 122° (from methyl alcohol). Under oxidation, 1,4-methyl-cyclohexanone is formed, in addition to which, oxalic acid and an acid sparingly soluble in benzene (m. p. about 140°) are formed. Dry distillation gives 1,4-methyl-methenehexane. The hydroxy-ester which is formed in the process of condensation of 1,4-methyl-cyclo-hexanone with α-bromo-propionic acid ester is readily saponifiable into methyl-cyclohexanol propionic acid, melting at 110 to 111° In addition

there occurs a small proportion of a second modification, which was not examined more closely.

When the acid melting at 110 to 111° is boiled with acetic acid anhydride, there results semicyclic 1,4-methyl-cyclohexane-propionic acid; when it is oxidised with permanganate of potassium, 1,4-methyl-cyclohexanone is formed. Dry distillation yields 1,4-methyl-cyclohexenethane (b. p. 152 to 153°, $d_{21°}$ 0,810; $n_{D21°}$ 1,4571).

When subjected to slow dry distillation, the same hydrocarbon yields methyl-cyclohexanol propionic acid, which melts at 110 to 111°. This forms a nitrosochloride (m. p. 108 to 110°, from ether and a little methyl alcohol), which, with piperidin, yields a nitrol-piperidide, m. p. 127 to 128°. Treatment with sodium acetate in glacial acetic acid produces the oxime of Δ^3-tetrahydro-p-acetyl-toluene, m. p. 117°.

By condensing cyclopentanone with bromopropionic ester, cyclopentanol propionic ester is obtained. The free acid melts at 58 to 59°. When the ester is treated with bisulphate the result is a mixture of cyclopentene propionic acids with isomeric bonds. When the free cyclopentene propionic acid is boiled with acetic anhydride, semicyclic cyclopentene-propionic acid, m. p. 107 to 108°, together with considerable proportions of hydrocarbons, results. Dry distillation yields ethylidene cyclopentane: b. p. 113 to 117°, $d_{20°}$ 0,8020, $n_{D20°}$ 1,4481, of which the nitrosochloride, when treated with piperidin, yields a nitrol piperidide, m. p 110°. When the nitrosochloride is boiled with acetate of sodium and glacial acetic acid there is obtained from it the oxime of acetyl-cyclopentene, m. p. 90 to 91° (from petroleum ether), m. p. of the benzoyl-combination 116 to 117°. When it is boiled with dilute sulphuric acid it yields acetyl-cyclopentene, of which the semicarbazone has a m. p. varying from 203 to 211°, according whether the heating is done slowly or rapidly. The ketone regenerated from the semicarbazone has a pronounced odour of benzaldehyde, and possesses the following constants: b. p. 173 to 174°, $d_{19°}$ 0,948, $n_{D19°}$ 1,4749.

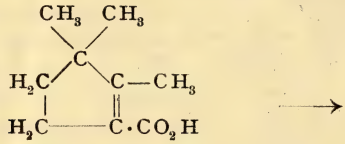
Besides the above, the isomeric ethyl cyclopentene with cyclic double-bond was formed. This had a b. p. of 107 to 110°, $d_{20°}$ 0,7975, $n_{D20°}$ 1,4426.

I. $(CH_2)_x\langle \begin{matrix} CH_2 \\ CH_2 \end{matrix} \rangle C(OH)\cdot CHR\cdot CO_2H$ (resp. $CO_2C_2H_5$)

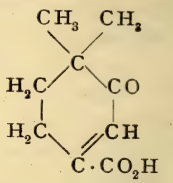
II. $(CH_2)_x\langle \begin{matrix} CH \\ CH_2 \end{matrix} \rangle C\cdot CHR\cdot CO_2H$

III. $(CH_2)_x\langle \begin{matrix} CH_2 \\ CH_2 \end{matrix} \rangle C{=}CR\cdot CO_2H$

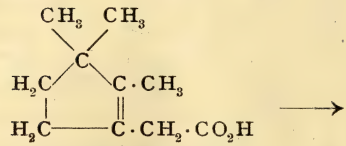
Perkin and Wallach [1]), in their paper on Δ^1-acetyl cyclopentene as the oxidation-product of Δ^1-cyclohexene acetic acid, laid stress upon the fact that the forming of an unsaturated pentacyclic compound was entirely unexpected and surprising, and that this showed how careful an investigator must be in drawing conclusions as to the constitution from oxidative decomposition with permanganate of potassium. Bouveault [2]) raises a few objections to this conclusion. In the first place he is of opinion that the formation of a cyclopentene derivative from a cyclohexene derivative, caused by the action of an alkaline solution of permanganate, cannot be regarded as in any way surprising, as a reaction producing reverse result has long been known, viz., the conversion of *iso*-lauronolic acid into *iso*-lauronic acid and that of β-campholenic acid into the *iso*phorone of camphor.



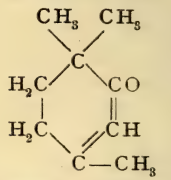
*Iso*lauronolic acid



*Iso*lauronic acid



β-Campholenic acid



*Iso*phorone of camphor

Secondly, and contrary to the view of Perkin and Wallach, Bouveault regards the application of the oxidation-process by permanganate for determining of the constitution of bodies as entirely justified in the case of hydrocarbons of the methylcyclohexene type, because Wallach only obtained 1 per cent. of keto-cyclopentene, while a rich yield had been obtained of the normal product of oxidation. Rearrangement, Bouveault thinks, is only to be expected when negative groups are found adjacent to the double-bond.

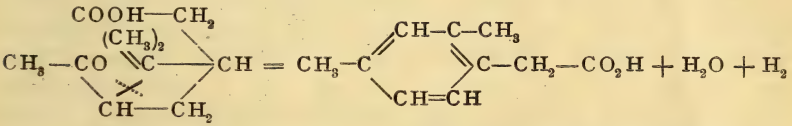
We have already previously reported on l-pinonic acid [3]) which has been prepared by us from oil of hyssop, as well as on the deri-

[1]) Berl. Berichte **42** (1909), 145; Report April **1909**, 137.

[2]) Ibidem **42** (1909), 1055.

[3]) Report April **1908**, 60; April **1909**, 137; Gildemeister and Köhler, Über das Vorkommen von β-Pinen und l-Pinocamphon im Ysopöl, und einige Beobachtungen über Isomerien in der Pinenreihe. Wallach Jubilee publ., p. 414. Vandenhoek and Ruprecht, Göttingen 1909.

vatives thereof obtained by Barbier and Grignard.[1]) The last-named authors[2]) have recently reported on a conversion of pinonic acid into dimethyl-1, 3-phenyl acetic acid. They observed this conversion while engaged in heating for 14 hours in an enamelled autoclave, at 100°, racemic pinonic acid with an equimolecular quantity of bromine and a quantity of water corresponding to the weight of the other materials, the object of the experiment being the preparation of the monobromo derivative of rac. pinonic acid. After neutralising with bicarbonate of sodium they precipitated carefully by means of diluted hydrochloric acid; brown flocculent masses being at first separated, while a lustrous crystalline deposit was next formed. This precipitate, recrystallised from water, melted at 101° and contained no bromine. It was a monobasic acid $C_{10}H_{12}O_2$ which was identified by the amide (m. p. 183°) and the methylester (b. p. 120 to 121°, 11 mm.) as dimethyl-1, 3-phenyl-acetic acid-4. The reaction takes place according to the following equation: —



Pinonic acid — Dimethyl-1, 3-phenylacetic acid-4

Campholic acid, of which so far only the dextro-rotatory form was known, has now also been obtained by M. Guerbet[3]) in the form of its lævo-rotatory isomeride, this result being obtained by heating l-borneol with freshly dehydrated potassium hydroxide in a sealed tube. A small proportion of *iso*campholate of sodium was formed as a bye-product.

L-campholic acid occurs in colourless crystals, m. p. 106 to 107°; b. p. 225° (760 mm.); $[\alpha]_{D\,15°}$ — 49° (in alcoholic solution). In order to identify it a series of salts and esters was prepared, as well as the anhydride (m. p. 57 to 58°), the chloride (b. p. 222°) and the amide (m. p. 77 to 78°).

Guerbet afterwards discovered that the borneol[4]) which had not been attacked had become partly converted into camphor. In this case a condition of equilibrium probably sets in, for the quantities of

[1]) Compt. rend. **147** (1908), 597; Report April **1909**, 120.
[2]) ibidem **148** (1909), 646.
[3]) Journ. de Pharm. et Chim. VI. **29** (1909), 225; Compt. rend. **148** (1909), 98.
[4]) Compt. rend. **148** (1909), 721; Bull. Soc. Chim. IV. **5** (1909), 418.

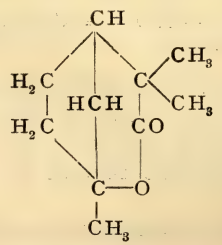
camphor and borneol varied according to the conditions under which the test was applied.

When Guerbet heated *iso*-borneol instead of l-borneol with potassium hydroxide, he obtained inactive campholic acid, which proved to be identical with the racemic product obtained from a mixture of d- and l-campholic acid.

Recrystallised from 80 per cent. alcohol, the inactive acid forms translucent hexagonal flaky crystals, m. p. 109°, whereas the two active acids form longish, clino-rhombic prisms, longitudinally striped.

	m. p.	Solubility	Sodium salt	m. p. of anhydride	m. p. of Amide
active campholic acid	106°	6,5 pts. in 10 pts. 80 per cent. alcohol	$C_{10}H_{17}O_2Na$, $5H_2O$	56°	78—79°
inactive campholic acid	109°	2 pts. in 10 pts. 80 per cent. alcohol	$C_{10}H_{17}O_2Na$, $8H_2O$	66°	90°

The lactone of α-hydroxy-dihydro fencholenic acid, a body difficult to obtain, has thus far only been prepared by roundabout methods. Recently, A. Blumann and O. Zeitschel[1]) observed that this lactone had been formed, although only in small proportions (1 to 2 %) when oxidising a large quantity of fenchylalcohol by means of Beckmann's chromic acid mixture. Contrary to expectation, it was impossible to prepare the lactone from fenchone by this process, for even after being treated with chromic acid mixture for 3 days at normal temperature, the fenchone remained wholly intact. For purposes of identification the authors prepared from hydroxy-dihydro-fencholenic acid lactone (m. p. 77 to 78°; $[\alpha]_D$ +17° 41′) the corresponding hydroxy-acid (m. p. 106 to 107°; $[\alpha]_D$ — 3° 13′), α-fencholenic acid (b. p. 144 to 146°, 12 mm.) as well as hydrochloro-fencholenic acid (m. p. 97 to 98°).



Lactone of α-hydroxy-dihydro-fencholenic acid

Cinnamic acid. The publication by Biilmann[2]), to which reference was made in our last Report, has been amplified by C. Liebermann[3]),

[1]) Berl. Berichte **42** (1909), 2698.
[2]) Berl. Berichte **42** (1909), 182; Report April **1909**, 140.
[3]) ibidem **42** (1909), 1027.

in a paper in which the author endorses Biilmann's theory on the trimorphy of the isomeric cinnamic acids. Referring to Biilmann's assertion that the cinnamic acids melting respectively at 38, 46, 57, and 68° are chemically identical, Liebermann points out, however, that the fact that separate modifications can exist within so wide a range of temperatures indicates that the differences between these bodies are not only crystallographical but also to some extent chemical. Liebermann moreover shows that mere mechanical manipulations, such as rubbing, may cause the acid melting at 42 to 43° to become converted into the variety melting at 65 to 66,5°. He also noticed that the *iso*-acid, m. p. 58°, especially after being comminuted, was con-te verted into the *allo*-acid, m. p. 68°, after prolonged exposure to light.

Meanwhile Biilmann[1]) has continued his earlier investigations and has been able to confirm the observations he has already made with regard to the ready conversion of the three cinnamic acids as well as his theory of a trimorphy of the three acids, although the behaviour of the acids melting respectively at 58 and 68° points to the existence between them of differences which up to the present have not yet been explained.

Without entering into details of the experiments, we desire to give a synopsis of the results of Erlenmeyer's[2]) most recent investigations, which form a continuation of this author's work to which we referred in our last Report[3]).

The author's investigations show that hetero-cinnamic acid can be formed in plants, although only in comparatively small proportions. As regards the cinnamic acids which are made by various synthetic processes, the heating of benzalacetone with sodium hypochlorite (according to the process of the Farbwerke Meister, Lucius and Brüning) produced mixtures of storacic and hetero-cinnamic acid. Heating of benzal-malonic acid with glacial acetic acid (Claisen's and Crismer's process)[4]) resulted in *allo*-cinnamic acid accompanied by similar acids, which separated out in the crystalline form of storacic and hetero-cinnamic acids. Cinnamic acid ester prepared according to Claisen[5]) and Erlenmeyer[6]) from acetic ester and benzaldehyde by condensation with sodium, yielded, when saponified, synthetic cinnamic acid. Phenylpropionic acid, when reduced with zinc-dust and glacial acetic acid (Aronstein's and Holleman's process)[7]), yielded storacic cinnamic

[1]) ibidem **42** (1909), 1443.
[2]) ibidem **42** (1909), 2649 and 2655.
[3]) ibidem **42** (1909), 502; Report April **1909**, 138.
[4]) Liebig's Annalen **218** (1883), 135.
[5]) Berl. Berichte **23** (1890), 977.
[6]) Liebig's Annalen **275** (1893), 12.
[7]) Berl. Berichte **22** (1889), 1181.

acid. Perkin's reaction, applied under various experimental conditions, such as different durations of the reaction, different proportions of benzaldehyde (origin not stated), sodium acetate and acetic anhydride, as well as increased temperature, always yielded the same synthetic cinnamic acid. In order to settle the point whether perhaps the cause of the differences in the cinnamic acids was to be sought in the benzaldehyde, a benzaldehyde free from chlorine was carefully distilled. In the course of frequently repeated fractionations the author succeeded in recovering a "volatile constituent" as well as one boiling between 182 and 184°. By Perkin's reaction, storacic cinnamic acid was obtained from the most volatile fraction (b. p. not stated), and hetero-β-cinnamic acid from the fraction with the highest b. p.

In order to prove the connection between the special properties of hetero-β-cinnamic acid and the aromatic nucleus, the former was oxidised with permanganate into benzaldehyde, and cinnamic acid regenerated from this product. The acid, again, was hetero-β-cinnamic acid. Natural banzaldehyde containing hydrocyanic acid yielded chiefly storacic-cinnamic acid. But when the aldehyde was split up into fractions boiling respectively at 150 to 178° (I), 178 to 180° (II), and 180 to 180,5° (III) and each fraction treated by itself, fraction I yielded storacic acid, fraction II synthetic acid, and fraction III hetero-β-cinnamic acid. This result indicates the probability that when hydrocyanic acid is eliminated from the natural benzaldehyde containing that acid, the benzaldehyde is converted into "synthetic" benzaldehyde. As a matter of fact, the aldehyde referred to above, when freed from hydrocyanic acid by our process, yielded synthetic cinnamic acid.

Erlenmeyer also mentions experiments for the reciprocal conversion of the different cinnamic acids. He found, *inter alia,* that storacic acid remains unaltered when boiled for 36 hours with caustic soda liquor, whereas on prolonged exposure in the cold in concentrated sulphuric acid it gradually becomes converted into hetero-β-cinnamic acid. In order to convert storacic cinnamic acid into the synthetic product, the former is oxidised into benzaldehyde with permanganate of potash, and from the latter, when condensed, synthetic acid almost always results. The discovery that with Perkin's reaction, but in the presence of copper, ordinary benzaldehyde yields storacic cinnamic acid, is a remarkable one.

A table containing data as to the manner in which storacic-cinnamic acid, synthetic cinnamic acid and hetero-β-cinnamic acid are obtained and generated, is added to the paper. The results of an examination of the crystallographic elements of the cinnamic acid dibromides and the conductivity of the isomeric cinnamic acids (this latter by K. Bube), are also given. The investigation is to be continued.

Nitrogenous Bodies.

Since indol and skatol have been known as constituents of essential oils, efforts have been made to determine the presence of these bodies by the clearest possible reactions. As stated in our last Report[1]) F. Weehuizen has utilized Steensma's colour-reaction of indol for the purpose of determining their presence. The process published by C. Gautier and T. Noyer[2]) is based upon the same principle, with the exception that chloroform is used for extracting. This method makes it possible to detect the presence even of traces of the two bodies referred to. 5 cc. of the liquid under examination are shaken up with 5 cc. of a 5% alcoholic solution of p-dimethylamido benzaldehyde, next diluted with 1 cc. of pure concentrated hydrochloric acid and the solution extracted with 5 cc. chloroform. If indol is present the chloroform assumes a carmine colour; if skatol, it turns blue[3]). In the presence of a mixture of the two bodies the chloroform acquires a violet tint. The spectra of the two colours also differ.

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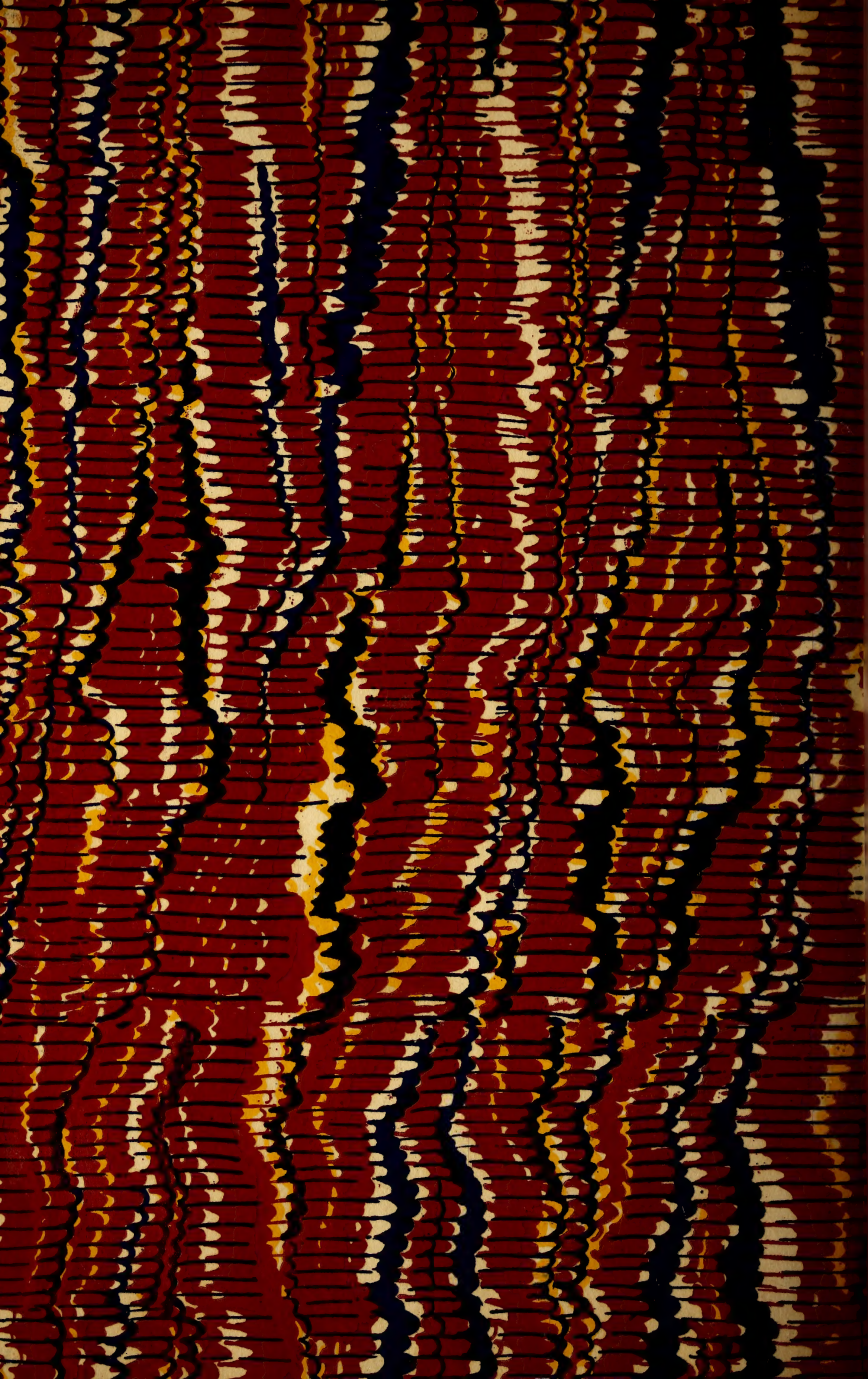
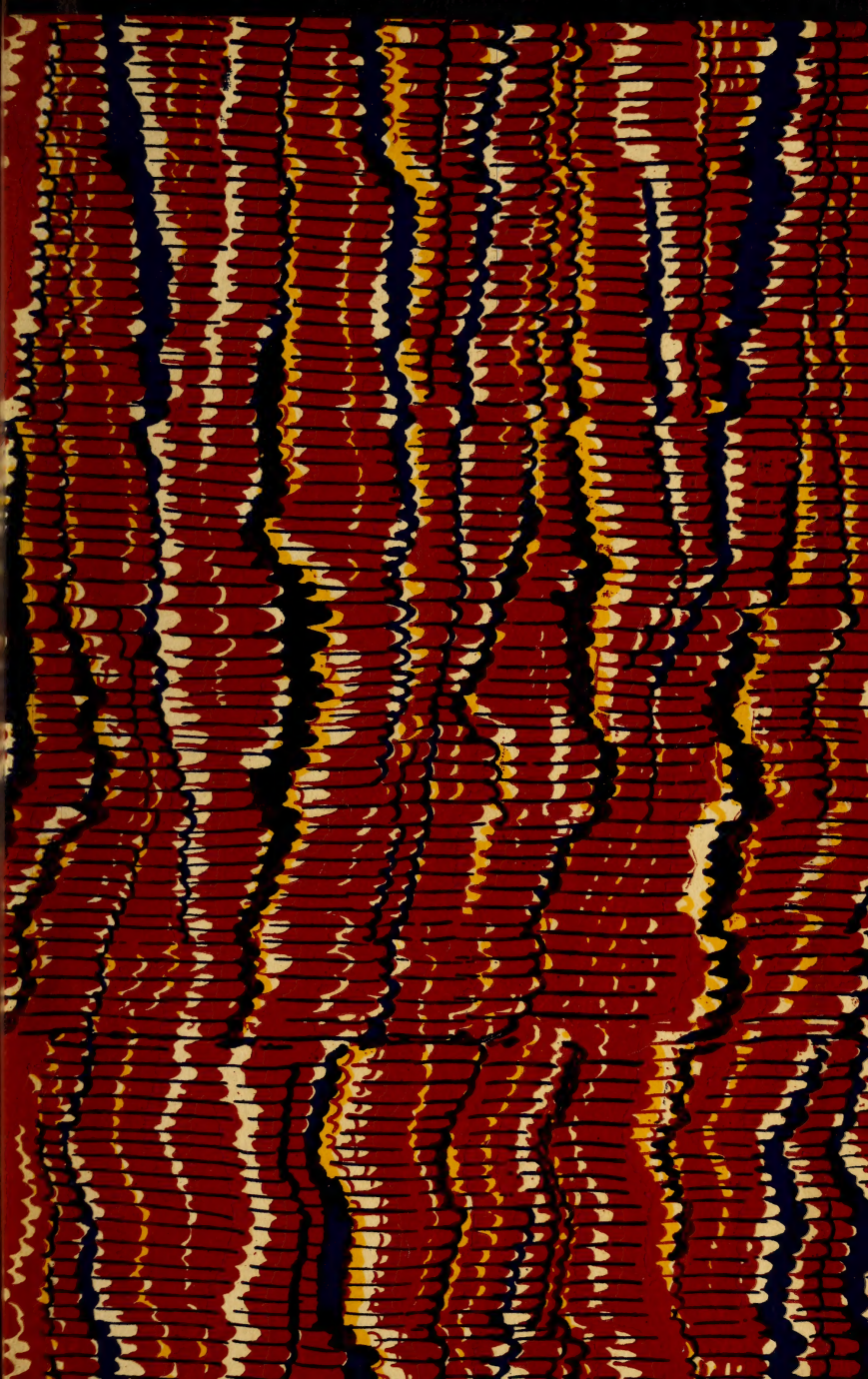
[1]) Report April **1909**, 140.

[2]) Compt. rend. soc. biol., 19 Dec. 1908. Quoted from Bull. Soc. chim. IV. 5 (1909), 256.

[3]) Weehuizen in his paper has already referred to this blue colouring.

J. J. Weber, Leipzig.





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